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ISSUE RESOLUTION STATUS REPORT

KEY TECHNICAL ISSUE:
RADIONUCLIDE TRANSPORT

Division of Waste Management
Office of Nuclear Material Safety and Safeguards
U.S. Nuclear Regulatory Commission

Revision 1

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Change History of "Issue Resolution Status Report (IRSR), Key Technical Issue: Radionuclide Transport"

Revision No.	Section/ Paragraph	Date	Modification
Rev0	all	December 1998	None. Initial Issue
Rev1	1.0/4, 6, & 7	June 1999	Clarification of relationship of radionuclide transport IRSR to 10 CFR Part 63, Yucca Mountain Review Plan (YMRP), and Department of Energy (DOE) License Application (LA)
Rev1	2.0/all	June 1999	Relationship of radionuclide transport IRSR to other KTI and IRSRs, updating status of subissue acceptance criteria
Rev1	3.0/3	June 1999	Updating to reflect application of Total-system Performance Assessment (TPA) code to radionuclide transport
Rev1	3.1/all	June 1999	Minor editorial
Rev1	3.2.1/all	June 1999	Minor editorial changes sections 3.2.1.1 through 3.2.1.4. New section 3.2.1.5 added to summarize DOE Total System Performance Assessment-Viability Assessment (TSPA-VA) approach to radionuclide transport
Rev1	3.2.2/all	June 1999	Minor editorial changes. New section 3.2.2.2.1 added to address importance of fracture transport. New section 3.2.2.2.2 to address radionuclide transport sensitivity analyses using TPA 3.2 code.
Rev1	4.0/all	June 1999	New introductory paragraph
Rev1	4.1.1/all	June 1999	Modified review methods

Change History of "Issue Resolution Status Report (IRSR), Key Technical Issue: Radionuclide Transport" (cont'd)

Rev1	4.1.2/all	June 1999	Minor modifications of section 4.1.2 in Rev0. Section numbering to clarify structure of technical bases. Updated to include summary of results from DOE tests at the C-wells complex and at Busted Butte, colloid transport of plutonium at the Nevada Test Site, and variable hydrochemistry
Rev1	4.2.1/all	June 1999	Minor modification to update references
Rev1	4.2.2/all	June 1999	Minor modifications to include preliminary results from Nye County Early Warning Drilling Program (EWDP)
Rev1	4.3.1/all	June 1999	Major modification to develop acceptance criteria for subissue on radionuclide transport through fractured rock
Rev1	4.3.2/all	June 1999	Major modification to reflect technical bases for revised acceptance criteria
Rev1	4.4.1/all	June 1999	Major modification to develop acceptance criteria for subissue on nuclear criticality in the far field
Rev1	4.4.2/all	June 1999	Major modification to reflect technical bases for revised acceptance criteria
Rev1	5.1.1/all	June 1999	Minor modification and reorganization to reflect TSPA-VA results. Updated to include summary of results from DOE tests at the C-wells complex and at Busted Butte, colloid transport of plutonium at the Nevada Test Site, and variable hydrochemistry

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Change History of "Issue Resolution Status Report (IRSR), Key Technical Issue: Radionuclide Transport" (cont'd)

Rev1	5.2.2/3	June 1999	Minor modifications to include preliminary results from Nye County EWDP
Rev1	5.3.1/all	June 1999	Major modifications to reflect revised acceptance criteria introduced in sections 4.3.1 and 4.3.2
Rev1	5.3.2/all	June 1999	Major modifications to reflect revised acceptance criteria introduced in sections 4.3.1 and 4.3.2
Rev1	5.4/all	June 1999	Major modifications to reflect revised acceptance criteria introduced in sections 4.4.1 and 4.4.2
Rev1	5.4.1/all	June 1999	Major modifications to reflect revised acceptance criteria introduced in sections 4.4.1 and 4.4.2
Rev1	5.4.2/all	June 1999	Major modifications to reflect revised acceptance criteria introduced in sections 4.4.1 and 4.4.2
Rev1	5.4.3/all	June 1999	New section to reflect progress in resolution and close out this subissue
Rev1	5.5/all	June 1999	Minor modifications and reorganization to clarify status of open items
Rev1	6.0/all	June 1999	Provide references for Rev1
Rev1	App. A/all	June 1999	Minor modifications to update summary of site-specific data

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ACKNOWLEDGMENTS FOR REVISION 0

This report was prepared by staff from the U.S. Nuclear Regulatory Commission and the Center for Nuclear Waste Regulatory Analyses (CNWRA). Primary authors of the report, in alphabetical order, are John Bradbury, Roberto Pabalan, English Pearcy, James Prikryl, and David Turner. The wives of the authors should be thanked for their understanding and generosity by sacrificing evenings and weekends for the IRSR. Also, the authors thank David Brooks, William Reamer, Michael Bell, and Wesley Patrick for their thoughtful reviews. Finally Carrie Crawford is offered a special thanks for her efforts in producing this report.

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This report has been prepared jointly by staff from the U.S. Nuclear Regulatory Commission (NRC) and the Center for Nuclear Waste Regulatory Analyses (CNWRA). Primary authors of the report, in alphabetical order, are John Bradbury (NRC), Roberto Pabalan (CNWRA), English Pearcy (CNWRA), David Pickett (CNWRA), James Prikryl (CNWRA), and David Turner (CNWRA). The authors thank David Brooks, William Reamer, Paul Bertetti, and John Russell for their thoughtful reviews. Finally, Arturo Ramos is offered special thanks for his efforts in producing this report.

QUALITY OF DATA, ANALYSES, AND CODE DEVELOPMENT

DATA: CNWRA-generated original data contained in this report meet quality assurance requirements described in the CNWRA Quality Assurance Manual. Sources for other data should be consulted for determining the level of quality for those data.

ANALYSES AND CODES: The computer code TPA Version 3.2, used to perform calculations presented in this report, has been developed following the procedures described in CNWRA Technical Operating Procedure TOP-018. The geochemical speciation codes MINTEQA2, Version 3.11 and PHREEQC, Version 1.6 were also used and are controlled under the CNWRA Software Configuration Procedures described in TOP-018. The spreadsheet software Microsoft Excel, Version 5.0, was also used in calculations presented in this report. This is a commercial spreadsheet software package and only the object code is available.

1.0 INTRODUCTION

The Commission has previously noted that, as part of the review of site characterization activities specified in the U.S. Nuclear Regulatory Commission's (NRC) geologic repository regulations, it contemplates an ongoing review of information on site investigation and site characterization activities, particularly those activities with long times to completion, so as to allow for the early identification and resolution of potential licensing issues. Moreover, NRC's strategic planning assumptions call for the early identification and resolution, at the staff level, of issues before the receipt of a potential license application (LA) to construct a geologic repository. The principal means for achieving this goal is through informal prelicensing consultation with the U.S. Department of Energy (DOE) in an open manner that permits observation by the State of Nevada, Tribal Nations, affected units of local government, and interested members of the public. This approach attempts to reduce the number of, and to better define, issues that may be in dispute after filling of a LA and during the NRC licensing review, by obtaining input and striving for consensus from the technical community, interested parties, and other groups on such issues.

Thus, consistent with NRC's regulations and a 1993 agreement with DOE, staff-level issue resolution can be achieved during the prelicensing consultation period; however, such resolution at the staff level would not preclude the issue being raised and considered during licensing proceedings. Issue resolution at the staff level during prelicensing is achieved when the staff has no further questions or comments (i.e., open items) regarding how the DOE program is addressing an issue. There may be some cases where resolution at the staff level may be limited to documenting a common understanding regarding differences in the NRC and DOE technical positions. Pertinent, additional information could raise new questions or comments regarding a previously resolved issue.

NRC's high-level radioactive waste (HLW) program was realigned during fiscal year (FY) 1996-1997. The realignment was in response to: (1) a reduction in Congressional budget appropriations for NRC in FY 1996; (2) the reorganization of DOE's geologic repository program at Yucca Mountain (YM), Nevada; and (3) a 1995 report issued by the National Academy of Sciences to advise the U.S. Environmental Protection Agency regarding the technical bases for new geologic disposal standards for YM. In response to these developments, the NRC HLW program was realigned to focus prelicensing work on those topics most critical to the postclosure performance of the proposed geologic repository; these topics are called *Key Technical Issues (KTIs)*. This approach is summarized in Chapter 1 of the staff's FY 1996 "Annual Progress Report" (Nuclear Regulatory Commission, 1997).

The current Division of Waste Management (DWM) approach is to focus most activities on issue resolution of the respective KTIs, at the staff level. DWM activities have been subsequently reprioritized, and organizations have been restructured to support, improve integration of, and streamline the technical work necessary to achieve staff-level resolution. Identifying KTIs, integrating their activities into a risk-informed approach that is consistent with the proposed rulemaking in 10 CFR Part 63, and evaluating their significance for postclosure repository performance helps ensure that regulatory attention is focused where technical uncertainties will have the greatest effect on the assessment of repository safety, and that all elements of the regulatory program are consistently focused on these areas. Early feedback among all parties is essential to define: (1) what is known; (2) what is not known; and (3) where additional information is likely to make a significant difference in the understanding of future repository safety.

An important step in the staff's approach to issue resolution is to provide DOE with feedback regarding issue resolution before the forthcoming LA. *Issue Resolution Status Reports* (IRSRs) are the primary mechanism that the NRC staff will use to provide DOE with feedback on KTI subissues. IRSRs focus on: (1) acceptance criteria for issue resolution; and (2) the status of resolution, including areas of agreement or when the staff has comments or questions. In addition, the NRC staff can send letter reports describing significant technical work toward resolution of KTIs. Finally, open meetings and technical exchanges with DOE provide additional opportunities to discuss issue resolution, identify areas of agreement and disagreement, and develop plans to resolve such disagreements.

In addition to providing feedback, the IRSRs guided the staff's review of information included in DOE's Viability Assessment (VA) (U.S. Department of Energy, 1998c). Also, the staff is currently using the IRSRs to develop the *Yucca Mountain Review Plan* (YMRP) for the DOE's repository LA. Current plans are to extract the acceptance criteria and review methods from the IRSRs and to consolidate them in the YMRP. To avoid problems with potential inconsistencies between the YMRP and the IRSRs, acceptance criteria and review methods will then be maintained only within the YMRP.

Each IRSR contains five sections. This 'Introduction' is Section 1.0. Section 2.0 defines the KTI, all the related subissues, and the scope of the particular subissues that are the subject of the IRSR. Section 3.0 discusses the importance of the subissue to repository performance including: (1) qualitative descriptions; (2) relationship to total system performance; (3) results of available sensitivity analyses; and (4) relationship to the DOE *Repository Safety Strategy* (RSS) (U.S. Department of Energy, 1998a,b), that is, its approach to the LA. Section 4.0 provides the staff's review methods and acceptance criteria, which indicate the technical basis for resolution of the subissue that will be used by the staff in subsequent reviews of DOE submittals. These acceptance criteria are guidance for the staff and, indirectly, for DOE as well. The staff's technical basis for the acceptance criteria is also explained in detail to further document the rationale for staff decisions. Section 5.0 concludes the IRSR with the status of resolution, indicating those items resolved at the staff level or those items remaining open. Open items will be tracked by the staff, and resolution will be documented in future IRSRs.

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2.0 KEY TECHNICAL ISSUE AND SUBISSUES

The primary objective of the Radionuclide Transport KTI is to evaluate the processes that may affect radionuclide transport from the repository to the biosphere. Transport through the engineered barrier systems in the nearfield environment is addressed in the Evolution of the Nearfield Environment (ENFE) KTI. There are three modes of transport that can deliver radionuclides to the biosphere. Radionuclides can be carried: (1) as dissolved, particulate, or colloidal material in advecting groundwater; (2) as volatile species in the gas phase; or (3) as constituents of ejecta of a volcanic eruption that intersects the repository. This version of the radionuclide transport IRSR will address radionuclide mobility in the groundwater only. Issues related to groundwater flow through the unsaturated zone (UZ) and saturated zones (SZ) are evaluated as part of the Unsaturated and Saturated Flow Under Isothermal Conditions (USFIC) KTI (Nuclear Regulatory Commission, 1998b). Radionuclide transport in the gas phase is not considered an issue based on recommendations of the National Academy of Science (National Research Council, 1995), to adopt a dose-based standard. Where dose is the issue of concern, it is considered that gaseous radionuclide release to the accessible environment will be sufficiently diluted through mixing in the atmosphere to pose negligible risk. Consideration of radionuclides in volcanic ejecta is covered in the Igneous Activity (IA) KTI.

A number of processes, such as sorption, dispersion, mineral precipitation, filtration, and radioactive decay may serve to reduce radionuclide concentration during groundwater transport. It should be noted that matrix diffusion and dilution, two other processes that can also reduce radionuclide concentrations along the flow path, are being evaluated in the USFIC KTI (Nuclear Regulatory Commission, 1998b).

The radionuclide transport KTI has been subdivided into four subissues that may affect repository performance. They are

- Radionuclide transport through porous rock
- Radionuclide transport through alluvium
- Radionuclide transport through fractured rock
- Nuclear criticality in the far field

Resolution of these subissues require an adequate characterization of the physical and chemical system at YM affecting radionuclide transport. The spatial distribution of flow environments encountered by the radionuclides that escape the waste repository are generally thought to involve fractured rock, porous rock, and then alluvium. As a matter of convenience, the order of subissues discussed in this IRSR reflects an increase in complexity or uncertainties. The first subissue addresses radionuclide transport in porous rock. This subissue includes consideration of accessibility of the sorbing minerals in the porous matrix by the radionuclide contaminants, and the filtration of colloidal and particulate contaminants. The second subissue relates to the transport of radionuclides through alluvium. This subissue requires consideration of the flow paths through the alluvium, the likely materials encountered by radionuclide-contaminated solutions leaving the fractured and porous rock of the SZ, and the processes affecting radionuclide transport. The third subissue involves in fractured rock where the possibilities for preferred pathways and limited radionuclide-rock interactions exist. The last subissue is concerned with criticality in the far field. This subissue encompasses consideration of mechanisms and conditions that could concentrate fissile material into a critical configuration in the geologic environment removed from the thermally perturbed region.

Review methods and acceptance criteria are provided in this revision of the radionuclide transport IRSR for reviewing DOE's evaluations of radionuclide transport, and how they will be used to assess the performance of a HLW repository. As noted in Section 1.0, however, these review methods and acceptance criteria will eventually be extracted from the IRSR and placed in the YMRP.

3.0 IMPORTANCE TO REPOSITORY PERFORMANCE

The performance of a HLW geologic repository is a measure of its ability to limit radiological exposures to the public. The proposed HLW geologic repository at YM is located approximately 30 km from the public currently residing in Amargosa Valley. As estimated in the NRC staff's Draft Rule to 10 CFR Part 63, "Disposal of High-Level Radioactive Wastes in a Proposed Repository at Yucca Mountain, Nevada," the individuals likely to receive the highest dose from radionuclides released from the YM repository within 10,000 yr after disposal will be members of a hypothetical farming community, located approximately 20 km from YM. These individuals comprise the "critical group" as defined in the Draft Rule.

Radionuclide transport is important to repository performance, because the public can be exposed to radioactive waste only if the waste is transported from the repository through the geologic setting to the critical group. The estimated or calculated dose to the critical group is directly related to the concentration of radionuclides in the transporting medium.

The staff is evaluating the performance of a proposed repository at YM through the use of model abstractions (Nuclear Regulatory Commission, 1995, 1999a,b). Radionuclide transport is an important aspect of these performance assessment (PA) evaluations. For example, using the Total-system Performance Assessment (TPA) code, version 3.1 to perform sensitivity calculations demonstrated that of the different alternative conceptual models considered, a model with no retardation in the geosphere resulted in the greatest mean annual peak dose at both 10,000 and 50,000 yr (Nuclear Regulatory Commission, 1999b). In developing and updating the NRC PA models, key elements of subsystem abstractions (KESA) are defined in the IRSR for the Total System Performance Assessment and Integration (TSPAI) KTI (Nuclear Regulatory Commission, 1998a) as those elements necessary for DOE to demonstrate repository performance. These elements are illustrated in Figure C-1 (Appendix C). The key elements considered in the radionuclide transport KTI are located in UZ and SZ flow and transport components of the geosphere subsystem. These elements concern retardation in fractures and matrix in the UZ and retardation in water-production zones of the SZ and alluvium. The elements are abstractions of the site performance that are incorporated into the NRC PA models. Efforts in the radionuclide transport KTI are directed at determining the validity and robustness of these abstractions. As described in Section 2.0, the radionuclide transport KTI has been divided into four subissues. The importance of each subissue to performance is described below:

- Radionuclide transport through porous rock—when radionuclides pass through porous rock, the interactions between the dissolved radionuclides and the rock surfaces (e.g., sorption) result in retardation of the velocity of the radionuclides relative to the velocity of groundwater. The large surface areas of the porous medium tends to enhance sorption and consequently retardation. Furthermore, for those radionuclides whose sorption reactions may be kinetically inhibited, the slower average linear velocities of groundwater flow in porous media as compared to fracture flow promote the solid-liquid interaction. If the radionuclides exist instead as particulates or as colloids, they may be filtered out as groundwater flows through the constricted pores of the matrix. Sorption of radionuclides on solids and filtration of radiocolloids and particulates in the matrix reduces the radionuclide concentration in the liquid, as described in the

RSS (U.S. Department of Energy, 1998a,b). However, the low permeabilities of the matrix of some hydrostratigraphic units at YM may make some rock inaccessible to radionuclide-contaminated water on the time frame of repository performance.

- Radionuclide transport through the alluvium—current conceptual models of the alluvium incorporated in PA reflect limited information concerning the physical and chemical conditions of alluvium. For example, in the NRC's TPA 3.1 (Nuclear Regulatory Commission, 1999a,b), the alluvium is assumed to be crushed tuff similar to the material used in batch sorption experiments. The model abstraction assumes flow as in a sand column driven by the hydraulic gradient. Furthermore, it is assumed there are no preferential pathways in the alluvium. This assumption has yet to be tested. However, the occurrence of cut and fill structures formed in the alluvium by braided streams as evident in the walls of Fortymile Canyon may suggest that preferred pathways exist in the alluvium with the potential to reduce mixing and dilution.

- Radionuclide transport through fractured rock—recent site characterization activities involving the radioisotopes ^{36}Cl and ^{3}H provide evidence suggesting fast pathways of groundwater flow through the UZ (Fabryka-Martin, et al., 1996; Yang, et al., 1998). These fast pathways are proposed to occur as a result of flow down faults and fractures. Also, responses from adjacent wells in large-scale hydrologic pump tests (C-Wells) suggest preferential pathways may exist in the SZ at YM (Geldon, et al., 1997). If preferential pathways exist from the repository to the critical group, performance may be adversely affected, because portions of the geologic barrier would be bypassed. Currently, the NRC PA efforts take no credit for retardation of radionuclides in fractures. The rationale for assigning no retardation in the fractures is based on the hypothesis that there is limited capacity for sorption along fractures, and average linear velocities in fractured rock are high, limiting time for interaction between the dissolved radionuclides and the sorbing minerals lining the fracture walls. However, the presence of specific fracture-lining minerals may provide significant opportunity for sorption of specific radionuclides. For example, manganese oxyhydroxides may strongly sorb plutonium, uranium, and americium; calcite may strongly sorb or coprecipitate neptunium (Triay, et al., 1996a,b, 1997). Furthermore, matrix diffusion may provide for radionuclide retardation in fracture flow conditions (Reimus and Turin, 1997). Matrix diffusion is considered in the USFIC KTI (Nuclear Regulatory Commission, 1998b). Uncertainty, with regard to the effectiveness of these processes, results in the identification of radionuclide transport in fractured rock as a subissue of the radionuclide transport KTI.

- Criticality in the far field—as a first approximation, it is expected that processes and conditions that disperse the fissile material will dominate over processes and conditions that would tend to reconcentrate fissile material into critical geometries in the far field. This assumption is reflected in the current NRC PA system code, which does not consider criticality. However, the TSPA-VA Methods and Assumptions Report (TRW Environmental Safety Systems, Inc., 1997) states nuclear criticality scenarios will be evaluated (see 3.3.1.4). There are some scenarios that could lead to criticality that may affect performance. For example, Bates, et al. (1992) found that plutonium released from glass waste forms exists predominantly as colloids. If colloidal plutonium could be efficiently filtered in nonwelded bedded units below fractured strata of the repository horizon, it could accumulate sufficient mass for criticality. Consideration of neutron sorbers or poisons, either contributed from the natural system or from the repository may be important. Differences in the mobility may lead to chromatographic separations of fissile material and poisons. A criticality occurring over a long time could produce increasing amounts of fission products and neptunium. Some of the radionuclides generated in a criticality event could be relatively mobile and, thus, could adversely affect performance. Furthermore, criticality could: (1) generate additional colloids, capable of transporting radionuclides unretarded; (2) affect the groundwater flow field; or (3) result in gaseous release of volatile radionuclides.

The subissues of the radionuclide transport KTI deal with radionuclide transport in the various hydrogeologic media anticipated to be along the path of contaminant migration from the nuclear waste repository to the public. All of the subissues relate to one of the major system attributes of the DOE RSS (U.S. Department of Energy, 1998a,b), and this relationship is discussed in more detail in Section 3.1. A review of selected aspects of previous PAs as they relate to the radionuclide transport subissues is given in Section 3.2. Finally, sensitivity analyses performed by the NRC and the Center for Nuclear Waste Regulatory Analyses (CNWRA) relating to radionuclide transport are discussed in Section 3.3.

3.1 U.S. DEPARTMENT OF ENERGY REPOSITORY SAFETY STRATEGY

In the RSS (U.S. Department of Energy, 1998a,b), DOE describes its approach to protect public health and safety after closure of a YM repository. As part of that strategy, DOE has identified four key performance attributes of the natural and engineered barriers to isolate waste sufficiently to protect public health and safety. These attributes are

- Limited water contacting the waste packages (WP)
- Long WP lifetime
- Slow rate of release of radionuclides from the waste form
- Concentration reduction during transport through engineered and natural barriers.

The radionuclide transport KTI deals exclusively with issues related to the fourth key performance attribute as applied to the far field. Transport through the nearfield environment is addressed in the ENFE KTI. The dose to the critical group is directly related to the concentrations of radionuclides in the groundwater. The RSS describes mechanisms that can reduce the concentrations of radionuclides as they migrate from the repository to the point of groundwater withdrawal. Heterogeneities along the flowpath and various transport processes can cause dispersion or spreading of the radionuclide plume. Depletion, defined in the RSS as processes that lead to the effective removal of radionuclides as potential contributors to dose, results from processes such as precipitation, sorption, and matrix diffusion of radionuclides from the advecting groundwater. For the removal of radionuclides to be effective, these processes should be relatively irreversible on a time-scale important to performance. Compensating processes, such as dissolution and desorption, transferring radionuclides from the immobile solid to the mobile liquid phase would have to be less effective. If depletion can delay the radionuclides reaching the critical group, the concentration of some of the contaminants in the plume (parents) will decrease due to radionuclide decay, while others (daughters) will in-grow. The relative toxicity of the parents and the daughters is important in determining dose or risk.

Besides depletion processes, the RSS describes dilution as a process that can reduce radionuclide concentrations and limit annual dose. If the flux of water through the repository is small relative to the flux passing under the repository in the SZ, it is possible that significant dilution will occur. When the small amount of water that leaches the waste in the repository reaches the SZ, it may mix with a large amount of SZ water. To demonstrate the degree of mixing, it will be necessary to determine the extent of dispersion of the plume over the flowpath. Stratification of the saturated system may suggest contaminant plumes will be restricted to zones adjacent to the water table. Channeling of flow through the SZ fractures will limit mixing volume and dilution. If mixing and dilution do not occur along the flowpath to the critical group, dilution may occur at the well where uncontaminated water along with contaminated water may be pumped. Dilution in the SZ and at the well-head is considered in the USFIC KTI (Nuclear Regulatory Commission, 1998b).

The DOE RSS provides a table describing the types of testing or analysis needed to demonstrate the validity of the hypotheses that lead to a reduction in radionuclide concentrations during transport. Part of that table is duplicated below:

Table 3-1. Information sources for testing hypotheses

Attribute	**Hypotheses to be tested**	**Type of Testing or Analysis**			
		Numerical Modeling	**Laboratory Testing**	**ESF/ *In situ* Observations and Testing**	**Surface-Based Field Testing**
Concentration Reduction of Radionuclides During Transport	13. Physical properties of barriers reduce concentrations during transport	✓✓	✓✓	✓	✓✓
	14. Chemical properties of barriers reduce concentrations during transport	✓✓	✓✓✓	✓	✓✓
	15. Lower volume flow in unsaturated zone will be diluted by higher volume flow in the saturated zone	✓✓	N/A	N/A	✓✓

A single check represents sources where DOE recognizes additional information will be needed to evaluate the hypothesis. A double check represents areas where significant information exists but additional testing or analysis is expected to improve and confirm current understanding. Three checks indicate areas where testing or analyses to support the current phase of the program are essentially complete, although performance confirmation requirements could lead to future additional work.

3.2 CONSIDERATION OF RADIONUCLIDE TRANSPORT IN PREVIOUS PERFORMANCE ASSESSMENTS

Past PAs have simulated radionuclide transport in similar ways with minor variations of the abstractions as improvements to site performance models are gleaned from new site characterization information. Unlike the transport subissues, the subissue of criticality in the far field has not been addressed in any previous PA. It is a new subissue to be addressed in future PAs. The PAs include efforts by DOE and its contractors and NRC and its contractor, the CNWRA.

3.2.1 Department of Energy Performance Assessments

3.2.1.1 TSPA 91: Initial Total-System Performance Assessment for Yucca Mountain

The first of a series of biennial PAs conducted by the Yucca Mountain Project (YMP) was Total System Performance Assessment (TSPA)-1991 (Barnard, et al., 1992). The analyses in this study simulated flow and transport in one dimension (1D) and two dimensions (2D) using distributions of hydrogeologic parameters based on site and analogue data. Two conceptual models for UZ flow were considered. They were the composite porosity model and the weeps model. The composite porosity model assumed that flow is shared between the rock matrix and the fractures because of capillary forces, whereas, the weeps model assumed that water flows in locally saturated fractures with no matrix/fracture interaction. The weeps-model calculations did not include retardation in the UZ. UZ groundwater flow and aqueous transport were modeled as 1D (vertical) and 2D (lateral diversion). The accessible environment was located 5 km from the repository. The modeling simulated repository performance for 10,000 yr with some simulations extending to 100,000 yr. Sorption coefficients (K_d) were selected using an expert elicitation involving one expert. The "minimum K_d approach" (Meijer, 1992) was used in which highly sorptive radionuclides, such as tin, plutonium, and americium, were assigned a constant K_d of 100 mL/g. Flow and transport in the SZ was modeled in a 1D single composite medium 3,000 m wide, 1,000 m deep and 5,125 m long.

For both the composite porosity model and the weeps model, the unretarded anionic radionuclides, ^{99}Tc and ^{129}I dominated release. Additionally, ^{79}Se, ^{234}U, and ^{237}Np provided a minor contribution to dose. However, neither model led to doses that exceeded the 1985 Environmental Protection Agency (EPA) standard cumulative release limits.

3.2.1.2 TSPA 93: Total System Performance Assessment for Yucca Mountain—SNL Second Iteration

The TSPA-1993 PA used some more realistic representations of the YM site (Wilson, et al., 1994). Among the improvements over TSPA-91 were a more geohydrologically representative model of the repository, a three dimensional (3D) geostatistically correlated stratigraphy, an expanded hydrologic data set, explicit consideration of future climates, discrete modeling of individual geologic stratigraphy in the SZ, and modification of retardation and sorption parameters. Radionuclide sorption coefficients were selected using an informal expert elicitation, involving three experts. Sorption parameters were constrained assuming the effects of groundwater geochemistry. TSPA-93 only used geochemical information in estimating probability density functions (PDFs) for K_d. This analysis did not explicitly incorporate geochemistry in the calculations. It was assumed that the water from well J-13 and the Paleozoic (UE-25p#1) aquifer bound the chemistry of the groundwaters at YM. Sorption was also dependent on rock type. The strata through which the radionuclides migrate were abstracted into four rock types: devitrified, vitric, zeolitic, and iron oxide. The iron oxide rock type represents WP corrosion products.

$$R_f = 1 + \frac{\rho_b}{n} K_d \tag{1}$$

Radionuclide retardation is related to K_d, the sorption coefficient by the equation: where R_f is the retardation factor, ρ_b is the bulk density, and n is the porosity. This equation is for saturated flow. For unsaturated flow, the moisture content, θ is substituted for n. Retardation by adsorption was assumed to occur only in the matrix, but because of a strong coupling between the matrix/fracture, radionuclides traveling in the fractures were eventually retarded in the matrix. Flow and transport in the UZ were simulated using the same abstractions as in TSPA-1991, (i.e., the composite porosity model and the weeps model). Groundwater flow and aqueous transport were modeled as isothermal and single phase. Flow was represented by Darcy's law, and transport was represented by generalized advective/dispersive equations. Like TSPA-1991, the accessible environment was 5 km from the repository and the PAs investigated both cumulative releases and dose results for periods of 10,000 to 1,000,000 yr. The calculated composite porosity doses were significantly larger than those from the weeps model. This was due to the failure of more WPs in the composite porosity model. The weeps model, on the other hand, predicted earlier peak doses due to the assumption that there was no retardation in the UZ.

As in TSPA-1991, all releases were below the EPA's 1985 standard. However, longer-term (>100,000 yr) peak doses for drinking water pathways were significantly above background. Like the TSPA-1991 results, the radionuclides that contributed the most to the dose when releases were low were ^{99}Tc and ^{129}I. These radionuclides are assumed to be unretarded. When the calculated releases were high, the major contributors were ^{237}Np followed by ^{234}U. Neptunium and uranium are poorly sorbed by tuffs but more strongly sorbed than technetium and iodine. High solubility of neptunium makes it important to performance. Plutonium, although one of the most abundant radionuclides in the source term, contributed little to the dose because it was significantly retarded in the conceptual model. However, this PA not consider colloidal formation and transport, which may play a role in plutonium mobility (e.g., the Benham detonation event on the Nevada Test Site (NTS), where plutonium traveled as a colloid more than a km through tuffs in 20 yr).

3.2.1.3 TSPA 95: U.S. Department of Energy Total System Performance Assessment 1995

TSPA 95 modeled radionuclide transport where all rock/water interactions that retard radionuclide migration are assumed to be consistent with a simple, equilibrium (infinite capacity), distribution-coefficient (K_d) model. The whole rock distribution coefficients were based on laboratory-derived data and the “minimum K_d concept” (Meijer, 1992). The K_d PDFs were similar to TSPA-93 with minor modifications to Pu, Np, U, Ra, Cs, Sr, Ni, Pa, and Se. They depend on the chemical and mineralogical nature of the hydrostratigraphic units for both the UZ and the SZ. The units were classified as vitric, devitrified, and zeolitic, as in TSPA 93.

This PA used a Markovian algorithm to simulate fracture-matrix interaction in the UZ. This abstraction randomly transfers mobile radionuclides between fracture and matrix, depending on the infiltration rate, saturation, and hydrostratigraphic unit. Higher infiltration rates and saturations favor fracture flow along with tightly welded units, whereas, lower infiltration rates and saturations, and nonwelded units favor matrix flow. While in the matrix, the radionuclide is retarded by sorption processes; while in the fracture, the radionuclide is unretarded and moves with the water.

The SZ model assumed a 1D equivalent continuum advective-dispersive system. Consequently, only longitudinal dispersion was considered, and there was no transverse dispersion. Given a Darcy velocity of 2.0 m/yr, a value consistent with current estimates, the SZ was not considered a significant barrier to radionuclide release although sorption was considered in the abstraction. However, in this PA, the SZ was considered important because of its dilution effect.

Performance was determined for time periods ranging from 10,000 to 1,000,000 yr. The radionuclides with the greatest releases to the accessible environment (5 km from the repository footprint) during the 10,000 yr time frame are ^{99}Tc, ^{14}C, ^{129}I, and ^{36}Cl. All of these radionuclides are nonsorbing, having a K_d of zero. Therefore, processes affecting radionuclide transport are important to repository performance over a 10,000 yr period. Radionuclides with nonzero K_ds are sufficiently retarded, such that they fail to reach the accessible environment in 10,000 yr. For the 1,000,000 yr PAs the most important parameter was the SZ fluid flux that acted to dilute the contaminant plume, and, thus, reduced the dose. Given that long time, the peak concentration (and dose) reached the accessible environment, so retardation was considered to be unimportant.

The PA determined annual doses to individuals at 5 and 30 km. The subissue of radionuclide transport in the alluvium did not exist before 1995, because the well from which the critical group would withdraw contaminated water was assumed to be completed in the tuff. The NRC staff estimates the alluvium/tuff contact at the water table (along the flowpath) to occur 13 km southeast of the repository between wells J-11 and J-12. In the TSPA-1995, the 30 km flowpath was used in a calculation that led to a decrease in radionuclide concentration as a result of dilution and dispersion.

3.2.1.4 TSPA 98: Total System Performance Assessment—Viability Assessment Methods and Assumptions

The DOE Methods and Assumptions (TRW Environmental Safety Systems, Inc., 1997) provides a good description of the model abstractions to be expected in TSPA-VA for UZ radionuclide transport and SZ flow and transport. The length of the flowpath has been changed from that selected in previous PAs to 20 km. At that location, some flowpaths may pass through the alluvium. The period of performance for the analyses is primarily from 10,000 to 100,000 yr with minimal analyses of a 1,000,000-yr time period.

For the UZ, the report recognizes important factors from previous TSPAs affecting flow and transport. These include: (1) the UZ percolation rate; (2) the partitioning of flow between matrix and fractures; and (3) sorption coefficients. The flow and transport is decoupled. A library of steady-state flow fields generated for various infiltration rates reflects uncertainties in hydrologic properties of the different stratigraphic units in the UZ. For each realization, a new flow field is selected and transport is simulated by using the FEHM particle tracker module. FEHM uses a dual permeability formulation representing interacting fractures and matrix continua throughout the UZ. Transport processes include: (1) advective and diffusive exchange between fractures and matrix; (2) sorption/desorption; (3) birth and death of colloids; and (4) colloid filtration. Important effects on abstractions of physical transport processes in the UZ include: (1) appropriate conceptual models for fracture/matrix interactions; and (2) the range and dependencies of parameters associated with (a) those interactions, (b) effects of both long- and short-term transient flow conditions, and (c) extent of lateral and longitudinal dispersion to be expected. Important considerations related to chemical interactions include: (1) the appropriateness of the minimum K_d approach; (2) the amount of sorption to be expected in fractures; and (3) the contribution of colloids to radionuclide flux. Finally, potentially important effects related to heterogeneities in the UZ include: (1) consideration of spatial distribution of infiltration; (2) areal variations in amounts and compositions of zeolites; and (3) appropriate scale of heterogeneities.

For the SZ, simulations utilize 3D steady-state flow modeling with an equivalent continuum and effective transport porosity. A convolution integral approach is used to pass the radionuclides from the UZ to the SZ to give a concentration history at 20 km. There are six subregions at the foot of the repository at the water table where radionuclides enter the SZ flowtubes. The effects of climate change on flow and transport are determined, but these changes are assumed to be instantaneous step functions. Issues related to SZ flow and transport have been identified in the report. For example, it is recognized that channelization of flow in the SZ could increase effective flow velocity and reduce dispersivity, matrix diffusion and retardation. Also, the hydraulic characteristics of faults are uncertain. Sensitivity studies are to be performed to test the effect of faults on performance if they act as large scale barriers or conduits. Other issues to be addressed are colloidal transport, dispersivity, matrix and fracture sorption, possibility of vertical flow and its effect on dilution, the effect of the chemical plume from the heated repository on the SZ flow and transport, and consideration for pumping scenarios.

In addition to the radionuclide transport abstractions testing, the report describes the potential for nuclear criticality and its effect on performance. Previous studies have shown that if a critical configuration were permitted to form, and other necessary conditions (sufficient nuclear fuel, presence of neutron moderators, absence of neutron absorbers, and favorable geometry) were maintained, the consequences of a criticality for 10,000 yr would be to increase the inventory of some long-lived mobile radionuclides and, thus, affect dose. However, this calculated increase amounted to only 5 percent above the original inventory before criticality (TRW Environmental Safety Systems, Inc., 1997).

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Nuclear criticality scenarios are considered in three localities: in-package, nearfield, and far field. Only the scenarios involving the far field will be addressed in the radionuclide transport KTI. The scenarios for criticality in the waste package and nearfield are covered in the Container Life and Source Term (CLST) and ENFE KTIs, respectively.

TRW Environmental Safety Systems, Inc. (1997) describes how potential nuclear criticality requires the reconcentration of transported solute or colloids of fissile material in the far field. One scenario involves the precipitation of uranium under reducing conditions. The example provided suggests that carbonaceous material could act to reduce and subsequently immobilize the uranium and moderate the neutrons to promote the chain fission reactions. Natural analogues to this reconcentration mechanism exist as uranium ore deposits in western United States. Another example described is the filtration of colloidal plutonium in nonwelded bedded units. Such units exist just below the fractured Topopah Spring, the proposed repository horizon. Accumulation of colloidal plutonium could continue unabated until the pores are plugged, at which point flow would stop. The last example described in the report involves fissile material precipitating in organic rich beds of Franklin Lake Playa. Under pluvial conditions, spring deposits may occur at the north end of Amargosa Valley, as they have in the past, and with probable occurrence of organic material act to reduce, precipitate, and accumulate fissile material at the surface.

3.2.1.5 TSPA-VA: Total System Performance Assessment—Viability Assessment

The methods and assumptions summarized in Section 3.2.1.4 were used in developing the DOE VA and the supporting TSPA-VA. Nine radionuclides (^{14}C, ^{99}Tc, ^{129}I, ^{79}Se, ^{231}Pa, ^{234}U, ^{237}Np, ^{239}Pu and ^{242}Pu) were tracked from the EBS through the UZ and SZ to a receptor location at 20 km. In the DOE VA (U.S. Department of Energy, 1998c) and the TSPA-VA (Civilian Radioactive Waste Management System, Management & Operating Contractor, 1998a, Chapters 7 and 8), these radionuclides are assumed to interact with the geologic setting only in the case of transport through the matrix in the fractured tuff of the UZ and SZ and in the alluvium. Due to lack of information on fracture mineralogy and relatively rapid travel times, it is assumed that there is no retardation (i.e., $K_d = 0$) in fractures for all nine radionuclides being tracked in PA. Sorption coefficients in the matrix were assigned probability distributions based on expert elicitations conducted for earlier TSPA efforts.

In the DOE TSPA-VA, the basis for the values used for alluvium sorption parameters (Civilian Radioactive Waste Management System, Management & Operating Contractor, 1998a, chapter 8, section 8.4.2, p. 8–54) for the suite of nine radionuclides is the compilation of Thibault, et al. (1990). For application of these parameters in the vicinity of YM, distributions were derived by assuming the presence of oxidizing conditions and the presence of at least five percent calcite. The sorption coefficients are also scaled by effective porosity (n_{effAL}) in the alluvium to define an effective sorption coefficient K_d such that:

$$\left(\hat{K}_d\right) = K_d \frac{n_{effAL}}{n_{AL}} \qquad (2)$$

The DOE performed sensitivity analyses using the TSPA-VA code to investigate the effects of uncertainty in sorption parameters on performance. Based on the current design, DOE sensitivity analyses indicate that repository performance is not affected strongly by uncertainty in matrix sorption for transport through the UZ. In the SZ, sensitivity analyses focus on the length of the alluvium path (0–6 km, Civilian Radioactive Waste Management System, Management & Operating Contractor, 1998a, Section 8.4.2, p. 8–51). This is considered to be a parameter of interest because of "...a larger sorption capacity for neptunium and selenium..." (Civilian Radioactive Waste Management System, Management & Operating Contractor, 1998a, Section 8.4.2, p. 8–51). Sensitivity analyses were not conducted to investigate the effects of uncertainty in alluvium sorption coefficients on performance. The effects of uncertainty in sorption of neptunium in the SZ volcanics was investigated using a sensitivity analysis, but the K_d for neptunium sorption in the alluvium was held constant at 10 mL/g (Civilian Radioactive Waste Management System, Management & Operating Contractor, 1998a, Section 8.5.2.3.2, p. 8–84 to 8–85).

Colloid transport was included for the first time in TSPA-VA. DOE recognizes that the transport velocity of radionuclides attached to colloids may be faster than that of dissolved radionuclides because colloids may travel in the faster parts of the flow paths, and colloids may sorb to host rock less than dissolved radionuclides. For example, DOE notes that one of the more significant findings in the TSPA-VA is that, under certain conditions, colloid-facilitated transport is moderately important to repository performance in the time period from 10,000 to 100,000 yr. Only plutonium was considered in its analysis of radionuclide transport by colloids. Plutonium is believed by DOE to be the radionuclide most likely to be affected by colloidal transport because it is a major part of the waste inventory, has low solubility, and high sorption onto host rock. Field evidence at the NTS also supports the rapid migration of plutonium with a colloid phase (Thompson, 1998; Kersting, et al., 1999). Colloid transport of plutonium is modeled with an effective retardation factor $\hat{R}_f$, using the expression

$$\left(\hat{R}_f\right) = \frac{R_f + K_c R_c}{1 + K_c} \tag{3}$$

where R_f is the retardation of aqueous plutonium, R_c is the colloid filtration factor ($R_c = 1$ for the no filtration case) and K_c is the unitless colloid partitioning coefficient such that

$$K_c = K_{dcol} \times C_{col} \tag{4}$$

where K_{dcol} is the plutonium sorption coefficient on the colloid phase and C_{col} is the concentration of colloids in the groundwater. For reversible sorption on colloids, a log uniform distribution of K_c is assumed in TSPA-VA, with a maximum of 10 and a minimum of 10^{-5} in both the UZ and SZ. In addition, the ratio of irreversibly sorbed plutonium colloids to reversibly sorbed plutonium colloids is modeled assuming a range of 10^{-10} to 10^{-4}, based on observations of the Benham blast site on the NTS (Thompson, 1998; Kersting, et al., 1999). In the far field, this irreversibly sorbed plutonium is treated as a nonsorbing, slowly diffusing contaminant (U.S. Department of Energy, 1998c, Volume 3, Section 3.5.2.4).

In the base case presented in the VA, the major contributors to peak dose rate at 10,000 yr are calculated to be the high-solubility, nonretarded radionuclides ^{99}Tc, ^{129}I, and ^{14}C. Other radionuclides do not become significant contributors to dose until later times of 50,000 yr or more. These include the poorly sorbed radionuclide ^{237}Np. At 100,000 yr, ^{99}Tc, ^{237}Np, and ^{129}I are the major contributors to peak dose rate. Colloidal contributions to dose also begin to become significant at times of about 100,000 yr or more. In the base case, ^{239}Pu breakthrough at 20 km occurs at about 1,500 yr due to rapidly transported, irreversible plutonium colloids. Early plutonium concentration is dominated by irreversible colloids up to about 50,000 yr where the amount of plutonium reversibly bound to colloids begins to dominate. At times of 100,000 yr, colloidal plutonium (mostly ^{239}Pu) comprises about two percent of the peak dose rate. At 1,000,000 yr, ^{237}Np contributes the most to dose, but plutonium (mostly ^{242}Pu) comprises about eight percent of the peak dose rate(U.S. Department of Energy, 1998c, Volume 3, Section 4.3.1.1).

3.2.2 NRC/CNWRA Performance Assessments and Sensitivity Studies

3.2.2.1 Iterative Performance Assessment Phase 2

This PA (Nuclear Regulatory Commission, 1995) used the NEFTRAN II code (Longsine, et al., 1987) to simulate flow and transport of radionuclides from the repository 5 km to the accessible environment. The conceptualization of flow and transport involved two side-by-side legs representing fracture and matrix flowpaths for each stratigraphic unit. The contributions of flow from fractures and matrix depended on a number of factors, including total flux, hydraulic properties of the matrix, and fractures. Spatial and temporal heterogeneities were not considered in the flow and transport abstraction. Simulations using the computer code DCM3D were used to estimate 1D unsaturated flow in a dual porosity continuum (one fracture continuum and one matrix continuum). Steady-state flow was modeled for each hydrostratigraphic unit to determine the fraction of the total flow that was in the matrix as a percentage of the saturated conductivity of the matrix. The retardation parameter was calculated as a function of K_d, grain density of the matrix, porosity of the matrix, and moisture content. Of these parameters, K_d, grain density, and porosity are sampled. The PDFs for K_ds were based on batch sorption experiments of crushed tuff (Meijer, 1990). The moisture content is calculated and depends on the flux in the UZ.

The major contributors to dose include ^{94}Nb, ^{210}Pb, ^{243}Am, and ^{237}Np. Niobium appears in this list because it was assigned a K_d of zero. At the time, no technically defensible information was found to support sorption characteristics of niobium. Lead-210 builds in as a daughter product of the ^{234}U series. Although the K_d for americium is significant, at high flux conditions, fracture flow conditions exist. It was assumed that there was no sorption in the fractures. Therefore, americium would migrate unretarded. The large inventory of americium, along with the unretarded transport under high flux conditions, led to a contribution to dose. Neptunium, as in other PAs, also contributed to dose as a result of its large inventory and low K_d.

3.2.2.2 Total-system Performance Assessment (TPA), Version 3.1—Sensitivity Analyses

The NRC and the CNWRA are currently working on issues regarding radionuclide transport that may affect site performance. For example, the CNWRA is developing response surfaces for the TPA 3.1.4. code that will relate radionuclide sorption to groundwater compositions throughout the YM region. The results of this effort should improve estimations of K_ds to be assigned in the alluvium. Earlier work had shown that the pH dependence of actinide sorption is similar for a wide variety of minerals, such as quartz, α-alumina, clinoptilolite, montmorillonite, amorphous silica, kaolinite, and titanium dioxide. When normalized to an effective specific surface area, the magnitudes of the sorption coefficients (at a specific pH, initial radionuclide concentration, and PCO_2) are the same for the different minerals. This sorption behavior may be useful for abstracting sorption coefficients measured in the laboratory to those expected in the flow paths in PAs. The earlier work involved single minerals. Future work will extend the studies to include multiple minerals, as expected in the far field. The improvements to the code as response surfaces will be used to test the sensitivity of PA to changes in groundwater chemistry.

Additionally, studies involving discrete feature modeling will be used to estimate radionuclide transport through fractured rock. The conceptual model includes limited connectivities and sorbing surface areas, and preferential pathways that tend to enhance radionuclide mobility. On the other hand, numerous fractures branch off the major conduits and act as sinks for the radionuclides. Movement into these "dead-end" features in the UZ can be via advection or diffusion. A comparison of radionuclide transport in a discrete feature model will be compared to transport in the dual continuum of the TPA system code to illustrate the effect of choice of conceptual models on performance.

Site characterization activities suggest that localized areas of mildly reducing conditions may exist in parts of the SZ (Ogard and Kerrisk, 1984; U.S. Department of Energy, 1999). Given that constant chemistry is required for the valid application of the equation that is used to calculate a retardation factor from a sorption coefficient, auxiliary modeling will test the effects of variable chemistry on radionuclide transport and concentrations. Also, in light of this new information, criticality in the SZ will be assessed. Finally, filtration of plutonium colloids in nonwelded tuffs below the Topopah Spring will be examined as a reconcentration process for far field criticality. Chromatographic separation of fissile material from neutron absorbers will be evaluated.

3.2.2.2.1 Radionuclide Transport through Fractured Rock

The use of the constant K_d approach for estimating radionuclide transport T is based on the assumption that flow and transport is through a homogeneous porous medium or continuum. The equation that relates R_f retardation to K_d is given above in equation (1). Freeze and Cherry (1979) define the retardation factor as

$$\mathbf{R_f} = \frac{\bar{\mathbf{v}}}{\bar{\mathbf{v}}_\mathbf{c}} \qquad (5)$$

where $\bar{\mathbf{v}}$ is the average linear velocity of the groundwater and $\bar{\mathbf{v}}_c$ is the velocity of the 50 percent midpoint on the concentration profile of the retarded constituent. Additionally, the average linear velocity is related to the specific discharge, **(v)** or Darcy flux by

$$\bar{\mathbf{v}} = \frac{\mathbf{v}}{\mathbf{n}} \tag{6}$$

Substituting equation (5) and (6) into equation (1) yields

$$\frac{\mathbf{v}}{\mathbf{n}\bar{\mathbf{v}}_c} = \mathbf{1} + \frac{\mathbf{r_b}}{\mathbf{n}}\mathbf{K_d} \tag{7}$$

and multiplying both sides by n yields

$$\frac{\mathbf{v}}{\bar{\mathbf{v}}_c} = \mathbf{n} + \rho_b\mathbf{K_d} \tag{8}$$

Solving for the velocity of the retarded constituent yields

$$\bar{\mathbf{v}}_c = \frac{\mathbf{v}}{\mathbf{n} + \rho_b\mathbf{K_d}} \tag{9}$$

Since n is normally much less than $\rho_b K_d$, at constant specific discharge, the effect of varying porosity on the velocity of the retarded constituent is small. So travel times for radionuclides are insensitive to changes in effective porosity. This finding is valid as long as the conceptual model is correct (i.e., transport through a homogeneous porous medium).

Consider two flow systems with the same specific discharge (Darcy flux) but with different numbers of conductive features, such as fractures. System 1 has one smooth planar feature and System 2 has 1,000. From Snow (1968) the flux is proportional to the number of conduits and the cube of their apertures. Consequently,

$$
\begin{aligned}
&q_1 = q_2\\
&q_1 \propto N_1 b_1^{\,3}\\
&q_2 \propto N_2 b_2^{\,3}\\
&N_1 b_1^{\,3} = N_2 b_2^{\,3}\\
&\frac{b_1^{\,3}}{b_2^{\,3}} = \frac{N_2}{N_1}\\
&\frac{b_1}{b_2} = \sqrt[3]{\frac{N_2}{N_1}} = 10
\end{aligned}
\tag{10}
$$

where b_i is the fracture aperture and N_i is the number of fractures in the flow path in System 1. The porosities of the two systems can be calculated by

$$
\begin{aligned}
&n_1 = N_1 L W b_1\\
&n_2 = N_2 L W b_2\\
&\frac{n_1}{n_2} = \frac{N_1}{N_2}\frac{b_1}{b_2} = \frac{1}{1000}(10) = 0.01
\end{aligned}
\tag{11}
$$

Consequently, the average linear velocity of the groundwater in System 1 is 100 times that of System 2.

$$\overline{v}_1 = 100\overline{v}_2 \tag{12}$$

The retardation equation from Freeze and Cherry (1979) for transport in fractured systems is

$$\frac{\overline{v}}{\overline{v}_c} = 1 + AK_A \tag{13}$$

where A is the surface area to void-space (volume) ratio for the fracture opening through which the solute is being transported. The surface area of System 1 is 0.001 that of System 2

$$A_1 = \frac{SA_1}{n_1} = \frac{0.001SA_2}{.01n_2} = 0.1A_2 \tag{14}$$

Rearranging equation (13) to solve for the velocity of the constituent in System 1 yields

$$\bar{v}_{c1} = \frac{\bar{v}_1}{1 + A_1K_A} = \frac{100\bar{v}_2}{1 + 0.1A_2K_A} \qquad (15)$$

Likewise, the velocity of the constituent in System 2 is

$$\bar{v}_{c2} = \frac{\bar{v}_2}{1 + A_2K_A} \qquad (16)$$

Dividing equation 16 by equation 15 yields the ratio of the velocities of the constituents in the two systems

$$\frac{\bar{v}_{c2}}{\bar{v}_{c1}} = \frac{0.9}{100(1 + A_2K_A)} + 0.001 \qquad (17)$$

The ratio of the constituent velocities is a function of the sorption term, A_2K_A, which if allowed to vary from 0 to infinity, would result in the variation of the ratio from 0.01 to 0.001.

Consequently, in a fractured medium, knowledge of both the fracture porosity and the number of conductive features that contribute to the flux are important in predicting the velocity of the constituent. In a HLW repository, conditions that might lead to exposures before a 10,000 yr regulatory limit must be identified. Equation 13, although valid conceptually, has not been experimentally verified. The difficulty in verifying this relationship may stem from the problem of determining surface area of fractures. It should also be noted that in the 90 m packed off interval of the C-Well tests (Reimus, et al., 1998), only two conduits are identified that contribute 79 and 14 percent of the flux.

3.2.2.2.2 Sensitivity Analyses Using TPA 3.2

Preliminary sensitivity analyses using the NRC/CNWRA TPA 3.2 code have demonstrated that of the different alternative conceptual models considered, an assumption of no retardation in the geosphere results in the highest mean peak annual dose for both 10,000 and 50,000 yr time periods (Nuclear Regulatory Commission, 1999b). In addition, recent analyses performed using site-specific data and geochemical sorption models (Turner, 1998; Turner, et al., 1999) have provided correlations among K_ds for Am, Np, Pu, Th, and U that are used in TPA 3.2 to simulate radionuclide transport through alluvium. Preliminary results using TPA simulations at 50,000 yr and a critical group location at 20 km suggest that incorporation of correlation among K_ds does have an effect on peak mean total effective dose equivalent (TEDE) for these five radioelements relative to doses calculated assuming uncorrelated K_ds. For 250 realizations, calculated peak mean TEDE assuming correlation among K_ds can be either higher or lower than the uncorrelated case, suggesting an additional level of uncertainty that should be considered in PA. Several other radioelements (e.g., ^{226}Ra and ^{210}Pb) present in the decay chain from ^{234}U also exhibit similar effects of K_d correlation.

Finally, TPA 3.2 has been used to simulate colloid transport of a given radionuclide as a nonsorbing, nondiffusing solute (Contardi, et al., 1999). The purpose of these trials is to provide a conservative bounding case for plutonium and americium colloidal transport, and to investigate the need to modify the TPA code. These preliminary simulations of colloidal transport have shown no increase in the peak mean TEDE at 20 km within a compliance period of 10,000 yr. However, at later times greater than 10,000 yr the peak mean TEDE from the colloidal models increased by over a factor of 60 from the base scenario case.

4.0 REVIEW METHODS AND ACCEPTANCE CRITERIA

The approach that recent PA efforts at YM have used to simulate radionuclide transport in porous rock involves first establishing a groundwater flow field. This flow field is generated as a result of hydrologic modeling of the YM system using site-specific parameters, and can be 1D, 2D, or 3D, depending on the purpose of the modeling effort and the available data. The flow field representing the spatial distribution of groundwater velocities is then adjusted by dividing the velocity vectors by the retardation factor, R_f, for each radionuclide, to yield the radionuclide velocity fields. Current approaches model the groundwater flow field as a dual continuum representing both fracture and matrix flow at every node in the system.

Review methods and acceptance criteria are listed for the Subissues identified in Section 2.0 of this IRSR. Technical bases for the acceptance criteria are provided for those subissues.

4.1 RADIONUCLIDE TRANSPORT THROUGH POROUS ROCK

4.1.1 Review Methods and Acceptance Criteria

The DOE (U.S. Department of Energy, 1998a,b) considers radionuclide transport a key performance attribute of the natural barrier system in the proposed repository. Retardation of radionuclides through alluvium constitutes a key element of the NRC subsystem abstraction for PA. The DOE must adequately estimate the transport characteristics of the YM site and appropriately consider radionuclide transport through porous rock in their assessments of repository performance. The review process should determine which transport processes have been addressed/assumed by DOE. The reviewer should identify first, if the selected retardation processes are appropriate to the YM system, and second, whether they are addressed adequately for those radionuclides of concern.

The following *Acceptance Criteria* apply to evaluating the DOE estimates and consideration of radionuclide transport through porous rock:

1. For the estimation of radionuclide transport through porous rock, DOE has

    a. Determined, through PA calculations, whether radionuclide attenuation processes such as sorption, precipitation, radioactive decay, and colloidal filtration are important to performance

    b. (i) Assumed K_d is zero and radionuclides travel at the rate of groundwater flow, if it has been found that radionuclide attenuation is unimportant to performance and it can be demonstrated that this assumption is conservative in this case, Acceptance Criteria 2 and 3 do not have to be met or; (ii) demonstrated that Criterion 2 or 3 has been met, if radionuclide attenuation in porous rock is important to performance, or if an assumption that K_d is zero in porous rock is not conservative.

2. For the valid application of the K_d approach, using equation (1) $R_f = 1 + \rho_b K_d/n$ (or $R_f = 1 + \rho_b K_d/\theta$), DOE has

    a. Demonstrated that the flow path acts as an isotropic homogeneous porous medium [see USFIC IRSR) (Nuclear Regulatory Commission, 1998b), deep percolation on the subissue describing methods of estimating matrix properties].

    b. Demonstrated that appropriate values for the parameters, K_d, n or θ, and ρ_b have been adequately considered (e.g., experimentally determined or measured)

    c. Demonstrated that the following assumptions (i.e., linear isotherm, fast reversible sorption reaction, and constant bulk chemistry) are valid.

3. For the valid application of process models affecting radionuclide transport such as surface complexation, ion exchange, precipitation/dissolution, and processes involving colloidal material, DOE has

    a. Demonstrated that the flow path acts as an isotropic homogeneous porous medium [see USFIC IRSR (Nuclear Regulatory Commission, 1998b), deep percolation on the subissue describing methods of estimating matrix properties].

    b. Demonstrated that values for the parameters used in process models are appropriate and sufficient

    c. (i) Demonstrated that the three implicit assumptions (see 2c) are valid, if process models are intended to yield a constant K_d for use in the retardation equation (equation 1); or (ii) determined transport in a dynamic reactive transport system model (e.g., PHREEQC, MULTIFLO, HYDROGEOCHEM, etc.)

4. Where data are not reasonably or practicably obtained, expert judgement has been used and expert elicitation procedures have been adequately documented. If used, expert elicitations were conducted and documented in accordance with the guidance in NUREG-1563 (Nuclear Regulatory Commission, 1996) or other acceptable approaches. It is important to remember that expert elicitation and sensitivity analyses are not to be used as a replacement for experimental and field data, where such data can be reasonably obtained.

5. Data and models have been collected, developed, and documented under acceptable Quality Assurance (QA) procedures (e.g., Altman, et al., 1988), or if data were not collected under an established QA program, they have been qualified under appropriate QA procedures.

4.1.2 Technical Bases for Acceptance Criteria

Calculation of the radionuclide velocity field in the SZ involves using equation (1), $R_f = 1 + \rho_b K_d/n$, first proposed by Vermuelen and Hiester (1952) to describe the velocity of dissolved ions in a flowing system relative to the velocity of the water carrying the ions (equation 5). Processes, such as ion exchange with and adsorption on solids, slow the movement of the ions. The ions spend part of the time on the immobile solid phase (e.g., sand grains) and part of the time in the moving water. Equation (1) is valid only if the following three implicit assumptions are considered to be appropriate:

- Linear isotherm (equivalent to a constant K_d) (Freeze and Cherry, 1979)
- Fast reversible ion exchange and adsorption reactions (Freeze and Cherry, 1979)
- Constant bulk chemistry (Meijer, 1990)

Furthermore, equation (1) applies to systems in which the water is in intimate contact with the solids as in a column of granular material (e.g., crushed tuff). Such a situation allows for the maximum interaction between dissolved solute and surface sorption sites. Attempts have been made to modify equation (1) to apply to conditions that exist in the geologic environment and at YM. For example, in the vadose zone, where the porosity is incompletely filled with water, the moisture content, θ, replaces porosity in equation (1). Conca and Triay (1996) provide one example that illustrates a general agreement between the K_d of selenium determined in an unsaturated flow experiment with that in a batch sorption test conducted under saturated conditions.

4.1.2.1 CRITERION 1: Estimation of Radionuclide Transport through Porous Rock

4.1.2.1.1 CRITERION 1a. Determine, Through Performance Assessment Calculations, Whether Radionuclide Attenuation Processes Such As Sorption, Precipitation, Radioactive Decay, and Colloidal Filtration Are Important to Performance

Performance assessment is an acceptable method for evaluating the importance of radionuclide attenuation processes on repository performance. Processes and conditions other than those listed above may be well established and, consequently, make the radionuclide transport processes unimportant. For example, groundwater flow could be so slow that radionuclide travel time exceeds the period of regulatory concern. In that case, determination of attenuation parameters would not be required. However, when other processes and conditions are uncertain, characterization of attenuation processes can be used to compensate for those uncertainties and provide a measure of assurance on the capacity of the repository to isolate waste.

4.1.2.1.2 CRITERION 1b. Assume K_d Is Zero and Radionuclides Travel at the Rate of Groundwater Flow. If it Has Been Found That Radionuclide Attenuation Is Unimportant to Performance and Demonstrated That this Assumption Is Conservative in this Case, Acceptance Criteria 2 and 3 Do Not Have to Be Met Or; (i) demonstrated That Criterion 2 or 3 Has Been Met, If Radionuclide Attenuation in Porous Rock Is Important to Performance or If an Assumption That $K_d = 0$ Is Not Conservative.

By assuming K_d is zero for radionuclides known to occur as positively-charged dissolved species, radionuclide travel time should not be overestimated. Only in those rare cases where the radionuclides travel faster than the groundwater would this assumption not be conservative. These cases include anion and colloid exclusion, where either the charge or the size of the radionuclide-bearing mobile entity causes it to be restricted to only the largest pores, whereas, water can move through both large and small pores. If the largest pores constitute connected pathways, the mobility of the anion or colloid is enhanced; if the largest pores are unconnected, filtration occurs. For those radionuclides known to occur as anions or colloids or for conditions where high concentrations of natural colloids are expected, an assumption of a K_d of zero would not be adequate. Further characterization to address the possibility of anion or colloid exclusion would establish the rate of radionuclide transport.

4.1.2.2 CRITERION 2: K_d Approach for Estimating Radionuclide Transport

4.1.2.2.1 CRITERION 2a. Demonstrate That the Portion of the Flow Path to Which Equation (1) Applies Acts as an Isotropic Homogeneous Porous Medium

According to Freeze and Cherry (1979) the retardation equation $R_f = 1 + \rho_b K_d/n$ (equation 1) was developed on an "empirical basis" by Vermuelen and Hiester (1952) for use in chemical engineering and was first applied to groundwater situations by Higgins (1959) and Baestlé (1967, 1969). Equation (1) was subsequently derived from the general transport equation that describes solute concentration changes as a function of time, distance, dispersion coefficient, water velocity, soil bulk density, porosity, mass of solute per unit dry mass of soil, and degradation of solute. Bouwer (1991) states that equation (1) is applicable to 1D, horizontal, single-phase flow in saturated, unconsolidated, homogeneous, porous media. For unsaturated flow, the porosity, n, is replaced by the moisture content, θ.

Bouwer (1991) provides a simple hypothetical example to show that if preferential pathways occur in porous media, the rate of solute transport can be significantly affected. In his example, when the cross-sectional area of preferential paths are 0.1 of the total cross-sectional area of the 1D flow system (termed "fingering ratio"), the rate of radionuclide transport was increased by a factor of 10. When the fingering ratio was 0.01, the radionuclide transport was increased 100 times. From the example, he concludes "that compounds with high K_d can still be relatively mobile in the underground environment."

There are numerous examples at YM suggesting that preferential flowpaths exist in both the SZ and UZ. Hydrologic pump tests at the C-Well complex indicate flow features may be 10 to 100 m apart (Geldon, et al., 1997; Reimus and Turin, 1997). For the UZ, studies involving ^{36}Cl distribution in the Exploratory Studies Facility (ESF) (Fabryka-Martin, et al., 1996) suggest isolated pathways (possibly through-going faults) from the ground surface to the repository horizon. Discrete fracture modeling (Anna, 1998) using geologic surveys of fractures within the ESF suggested that the fracture network was sparse (possibly suggesting the fingering ratio is small).

The evidence for preferential pathways at YM coupled with the example from Bouwer describing the effect of preferential pathways on radionuclide transport provides the technical basis for this acceptance criterion. Currently, there are experiments (Bussod and Turin, 1999; U.S. Department of Energy, 1998c, Volume 1, Appendix C) planned at the Unsaturated Zone Transport Test Facility on Busted Butte located about 5 km south of the potential repository, that are designed to address the following PA needs:

- Confirm the validity of the dual permeability UZ transport process models,
- Validate the laboratory databases on sorption and matrix diffusion,
- Confirm the validity of the minimum K_d approach at the field scale,
- Assess the role of heterogeneities such as fractures in the Calico Hills formation (e.g., fracture matrix interaction within the Calico Hills nonwelded tuff),
- Investigate colloid mobility in fractured welded and nonwelded rocks,
- Determine fracture flow and transport mechanisms in unsaturated rocks,
- Investigate the effect of permeability contrasts at welded/nonwelded contacts and,
- Develop testing capabilities for possible future experiments beneath the repository horizon (i.e., east-west (EW) drift extension).

The DOE tests planned at Busted Butte may provide information to support the demonstration that the Calico Hills nonwelded unit acts as a porous medium. Phase 1 experiments include a 5-mo reactive and nonreactive tracer tests in the nonfractured upper Calico Hills Formation, and in the fractured Calico Hills below the basal vitrophyre of the Topopah Springs Tuff. Phase 2 tests are longer (13- to 18-mo) reactive and nonreactive tracer tests in a 10 × 10 × 6 m underground test block (U.S. Department of Energy, 1998c, Volume 1, Appendix C). Nonreactive tracers include potassium iodide, pyridone, and five separate polyfluorinated benzoic acids. Polystyrene latex microspheres are being injected to investigate colloid movement, and a number of reactive tracers such as nickel, molybdenum, cerium, and rhenium are being injected as analogs for radionuclide transport. Phase 1a experiments (unfractured Calico Hills) started in April 1998, and Phase 1b (fractured Calico Hills) started in May 1998. Phase 2 work has included characterization and instrumentation of the block, and Phase 2a tracer injection began in July 1998. Modeling studies predict that nonreactive tracer breakthroughs should occur within a year, while sorbing tracers should not reach the sampling locations for more than 1 yr. Extrapolation of the properties and fracture spacing of the Calico Hills nonwelded tuff at Busted Butte to YM will require further verification.

Other possible methods for demonstrating porous media flow may include:

- Showing that the effective porosity is approximately the total porosity at the expected flow rates and at the scale of the modeled flowpath at YM

- Determining the homogeneity of dye distribution on pore surfaces of an intact porous rock saturated with dye

- Demonstrating for unsaturated flow that conditions do not lead to fingering or preferential flow

- Performing hydrologic pump tests for the purpose of demonstrating the extent of preferential paths

Some of these methods have already been used to characterize the flow medium at YM, whereas others may be included in plans for future testing.

4.1.2.2.2 CRITERION 2b. Determine Appropriate Values for Parameters, K_d, n or θ, and ρ_b

Hydraulic properties at YM are currently being evaluated as part of the USFIC KTI (Nuclear Regulatory Commission, 1998b).

4.1.2.2.2.1 Sorption Coefficient, K_d

A list of methods acceptable to the staff and conditions for determining appropriate values of K_d is given below, followed by the technical bases for these suggested methods:

- Experimentally determine K_d from batch sorption tests using site-specific materials; experiments should be carried out to steady state.
- Site-specific solids to be used in the batch sorption tests are those that have been identified and characterized along the expected flowpaths radionuclides will travel from the repository to the critical group
- Methodologies of characterization should be appropriate for identifying and quantifying solids important to sorption (e.g., EXAFS, XRD, autoradiography, etc.)
- Site-specific groundwaters to be used in the batch sorption tests are those that have been identified and characterized along the expected flowpaths radionuclides will travel from the repository to the critical group; the groundwater-solid systems should be consistent with site data and bounding chemistry must be proved. For example, the reported pH of J-13 and UE-25p#1 is 6.9 and 6.7, respectively. The UZ pH, however, is up to 7.5, and in the SZ hydrochemical compilation of Perfect, et al. (1995), reported pH ranges from about 5.3 to >11. In addition, the pH of J-13 has been shown to vary over time from 6.8 to 7.6 (Oliver and Root, 1997).
- Perform confirmatory experiments such as crushed tuff column tests, intact core, diffusion slabs and cells and field tests
- Use process modeling to calculate constant K_d consistent with site data
- Use minimum K_d approach to calculate retardation but explain causes for experimental inconsistencies

Experimentally Determine K_d from Batch Sorption Tests Using Site-specific Materials

Acceptable methods for determining sorption coefficients involve experimentally determining K_ds from batch sorption tests using site-specific materials; experiments should be carried out to steady state. The technical basis for determining K_d experimentally stems from the observation that this parameter, for some radionuclides, can be sensitive to mineralogy and groundwater chemistry. For example, the K_d for plutonium on vitric tuff ranges up to 2,000 mL/g, whereas, for devitrified tuff, it can be as low as 20 mL/g. Furthermore, plutonium sorption on individual minerals can range from >10,000 mL/g on synthetic hematite to <10 mL/g on quartz (Triay, et al., 1997). Finally, prediction of K_ds from non site-specific studies can be uncertain. For example, the range of K_ds for selenium on sand range from 36 to 70 mL/g (Sheppard and Thibault, 1990), whereas, that measured on nonwelded zeolitic tuff was 0.08±0.2 mL/g (Triay, et al., 1997).

If radionuclide transport is modeled using the constant K_d, then batch sorption experiments should be carried out to steady state. Failure to reach steady state could be the result of an experimental problem, a competing process other than sorption, or a sorption reaction that is kinetically inhibited. Any of these possibilities would make the application of the K_d value in equation (1) suspect. For example, Figures 22–28 from Triay, et al. (1997), illustrate that plutonium batch sorption experiments had not reached steady state in a month. Although steady state had not been reached "...the sorption of plutonium on tuffs and minerals is very substantial" (Triay, et al., 1997). However, the breakthrough for plutonium and tritium in crushed tuff column experiments were comparable although complete recovery of plutonium was not attained (Figure 98 through 111, Triay, et al., 1997). The discrepancy between the results of the static batch sorption experiments and the dynamic column experiments suggests the complexity involved in characterizing plutonium transport.

Site-specific Solids

Acceptable methods for determining appropriate sorption coefficients involve the use of site-specific solids in batch sorption tests. These solids are those that have been identified and characterized along the expected flowpaths radionuclides will travel from the repository to the critical group. Some methodologies of characterization appropriate for identifying and quantifying solids important to sorption include EXAFS, XRD, autoradiography, SEM, EM, petrographic analysis, etc., Smyth, et al. (1980) concludes, using microautoradiography, that "it is possible for a minor phase to completely dominate the sorption properties of some rocks, as in the case for clay alteration in granites. In general, the hydrous secondary phases have very much larger sorption potentials than do anhydrous primary igneous minerals." As discussed above, the sorption experiment should use site-specific solids to reduce uncertainty with regard to the measured sorption coefficients.

At YM, the minerals encountered by fluids will vary depending on whether flow is through the fractures or the matrix (Bish and Vaniman, 1985). In the matrix, primary phases include glass and the minerals, quartz, alkali feldspar, cristobalite, tridymite, biotite, and hornblende. Secondary alteration minerals include zeolites, clays, calcite, opal, and chlorite. Thick layers of zeolitized (primarily clinoptilolite) tuffs in the Calico Hills and Prow Pass formations between the proposed repository horizon and the water table are expected to provide radionuclide retardation in the case of migration through the rock matrix (U.S. Department of Energy, 1988, Chapter 4). Several summaries of mineralogy have been developed, including Bish, et al. (1996) and Vaniman, et al. (1996a). Appendix A contains details of the matrix mineralogy at YM.

Site-specific Groundwaters

Acceptable methods for determining appropriate sorption coefficients involve the use of site-specific groundwaters in batch sorption tests. These waters are those that have been identified and characterized along the expected flowpaths that radionuclides will travel from the repository to the critical group. The water chemistry will exert significant control on radionuclide transport through the geosphere. Triay, et al. (1997) have studied the effects of groundwater composition on radionuclide sorption. The majority of the experiments were conducted using water from J-13 or UE-25p#1. Meijer (1992) proposes that these two groundwaters seem to bound water chemistry at YM. Additionally, the batch experiments were conducted in a CO_2 glovebox to maintain elevated PCO_2, or in the ambient atmosphere. At elevated PCO_2, the pH of J-13 and UE-25p#1 is ~7. At the atmospheric conditions of Los Alamos, the equilibrium pH is 8.5 for J-13 and ~9 for UE-25p#1.

Significant effort has been expended by DOE to characterize the water chemistry of the UZ, the SZ, and the perched water bodies in the YM vicinity (Appendix B). Summaries of UZ water chemistry are available in sources such as Yang, et al. (1996a,b, 1998). Hydrochemistry in the SZ is summarized in several studies, including McKinley, et al. (1991), Perfect, et al. (1995), and Oliver and Root (1997). The tuffaceous aquifer groundwater is a dilute, generally oxidizing, sodium bicarbonate solution rich in dissolved silica, although there are local reducing environments (U.S. Department of energy, 1999). Aquifers in the Paleozoic carbonate aquifers tend to be higher in total dissolved solids (TDS), and are dominated by calcium, magnesium, and aqueous carbonate dissolved from the carbonate rocks. Water from the alluvial aquifers can be high in TDS where evaporation has concentrated readily dissolved salts in playa deposits, but typically reflect the chemistry of the alluvium (carbonate versus tuff). The UZ tuffaceous matrix groundwaters differ substantially from SZ water, being more concentrated and dominated by calcium chloride or calcium sulfate in rocks nearer the ground surface (Yang, 1992; Yang, et al., 1993, 1996a,b, 1998). Aqueous silica concentrations in excess of cristobalite saturation are observed in tuffaceous aquifers at YM (Kerrisk, 1987), and higher concentrations are observed in the UZ (Yang, et al., 1996a). The high silica contents are generated by reaction of infiltrating meteoric water with siliceous volcanic glass (White, et al., 1980).

Recent studies (Turner, 1998; Turner, et al., 1998b, 1999), using the database of Perfect, et al. (1995) from which entries had been screened and culled based on a number of criteria, provides a systematic analysis of the range of compositions of groundwaters that could be encountered in the YM region. Parameters considered to be important to sorption and radionuclide transport were pH, total inorganic carbon, aqueous silica concentration, along with ionic strength, PCO_2, and saturation indices. From the initial 3,733 analyses, 460 analyses remained after the screening. Most samples that were eliminated lacked important chemical information, like pH, or Ca or HCO_3 concentration. It was found the pH ranged from 6.3 to 9.6. Total inorganic carbon ranged from 6.8 to more than 10,000 mg/L. Aqueous silica ranged from 2 to 130 mg/L. Ionic strength ranged from 4.34×10^{-4} to 1.3 molal. The partial pressure of CO_2 ranged from $10^{-5.08}$ to $10^{-0.77}$ atm. Saturation indices for calcite, Fe-oxides, cristobalite, and gypsum suggested that most waters are saturated with calcite, all with Fe-oxides, half the waters are saturated with cristobalite, and none are saturated with gypsum. The area covered by this dataset (UTM coordinates 4,000,000N to 4,100,000N and 500,000E to 600,000E) is much larger than the area typically considered in the TSPA-VA. In addition, the chemistry of wells may change over time. For example, the pH of J-13 has been shown to vary from 6.8 to 7.6 over a period of 30 yr (Oliver and Root, 1997). The variabilities observed in the region around YM suggest that the proposition that J-13 and UE-25p#1 bound chemistries expected at YM should be demonstrated.

Perform Confirmatory Experiments Such as Crushed Tuff Column Tests, Intact Core, Diffusion Slabs and Cells and Field Tests

Triay, et al. (1996b) describe the confirmatory experiments performed at Los Alamos National Laboratory (LANL) on YM materials to test the validity of the K_d values derived from batch sorption experiments. The objective of these experiments is to better simulate the conditions expected in the field at YM and compare the sorption coefficient from those experiments to that from the batch test. Batch tests are simple and relatively inexpensive to run compared to crushed tuff flow through experiments, saturated and unsaturated intact rock experiments, diffusion slab and cell experiments, and field tests. However, the static equilibration of radionuclide-bearing groundwater with crushed tuff may approximate a condition that is unexpected at YM. The use of dynamic experiments like the column tests can address concerns about kinetically inhibited sorption reactions or speciation reactions. Triay, et al. (1996b) provide a good discussion of the goal of the dynamic transport studies—"to test the necessary assumptions made in using values of K_d (determined by batch-sorption measurements) to describe hydrologic transport. These assumptions are:

- Microscopic equilibrium is attained between the solution species and the adsorbate,
- Only one soluble chemical species is present (or if more than one is present, they interchange rapidly),
- The radionuclides in the solid are adsorbed on mineral surfaces (that is, they are not precipitated), and
- The dependence of sorption on concentration is described by a linear isotherm."

Triay, et al. (1996b) continues "...The importance of verifying these assumptions can be demonstrated by the following hypothetical cases. If equilibrium were not attained in the batch experiments (violation of Assumption 1), the retardation of radionuclides could be dependent on groundwater velocity. If a radionuclide were present in solution as an anionic and a cationic species and solution equilibrium were not maintained (violation of Assumption 2), the batch measurement would predict a single retardation factor, whereas, in the flowing system, the anion could move unimpeded (its size and charge excluding it from the pores of the YM tuff) compared to the movement of the cation. If the radionuclide had precipitated in the batch experiments (violation of Assumption 3), the value of the K_d thus determined would be meaningless, and depending on the precipitation mechanism, colloid transport could be important. If the isotherm was nonlinear (violation of Assumption 4), the migration front of the radionuclides in a column study would usually broaden, appearing as increased dispersion over that observed for nonsorbing tracers." As an example, Triay, et al. (1996b) demonstrated that neptunium sorption results from crushed tuff column experiments agreed well with the batch sorption experiments.

Additionally, dynamic transport studies involving intact rock experiments eliminate the uncertainty about fresh surfaces of crushed tuff sorbing excessive amounts of radionuclides. Conca and Triay (1996) showed that the Unsaturated Flow Apparatus (UFA) could be used to determine the transport of selenium through unsaturated intact rock. The K_d derived from the flow-through experiment agreed with that determined by a batch sorption using the same materials.

Use Process Modeling to Calculate Constant K_d Consistent with Site Data

The use of process models is considered an acceptable method for estimating a constant K_d. See technical bases supporting Criterion 3.

Use Minimum K_d Approach to Calculate Retardation but Explain Causes for Experimental Inconsistencies

The minimum K_d approach was proposed by Meijer (1992) to compensate for uncertainties with experimentally derived K_ds from different tests and materials and potential variability in hydrochemistry. He proposed that the K_d value to use in calculating a retardation factor for a particular hydrostratigraphic unit be the smallest K_d for all the tests using material from anywhere in that unit. For this approach to be acceptable, sampling and testing of the hydrostratigraphic unit would need to capture the variability of the unit. In addition, an explanation for the experimental inconsistencies should be provided. The reason for the inconsistencies may provide a clue as to the mechanism of transport through the porous rock or the experimental problems that may have occurred but gone unrecognized.

4.1.2.2.2.2 Porosity, n, or Moisture Content, θ

Both the total porosity and the effective porosity should be determined for the porous rock. A large difference in these two numbers might suggest that the radionuclides have limited access to all parts of the porous medium. As a result, retardation may be decreased. Furthermore, effective porosity may be a function of flow rate or scale. As faster flow rates are imposed, only the most permeable conduits contribute to the flow. Likewise, as the flow rate decreases, those conduits that were considered stagnant at the higher flow rate, are now part of the flow system. Also, effective porosity may be a function of flow direction. For example, a tuff with flattened lapilli might have greater horizontal effective porosity than vertical effective porosity. Matrix properties and hydraulic parameter estimates are considered as part of the USFIC KTI (Nuclear Regulatory Commission, 1998b).

In porous media, experimental evidence indicates that solute dispersion is dependent on the degree of saturation. Barnes (1989) suggested that where hydraulic conductivity was modeled as a function of solute concentration, solute and moisture plumes separated more rapidly than for the case where hydraulic conductivity was considered to be independent of solute concentration. Calculations based on experiments for nonreactive solute transport through saturated and unsaturated columns of glass beads indicate that, at the scale of the experiments (3 m), dispersion increased much more rapidly with increasing pore water velocity under unsaturated conditions relative to saturated transport (de Smedt and Wierenga, 1984). For example, at pore water velocities of 500 cm/day, the calculated dispersion coefficient (D) was about 15 cm^2/day under saturated conditions, but approached 250 cm^2/day for unsaturated conditions. While this leads to greater spreading of a solute plume migrating through the UZ at a given velocity, slower water velocities can offset or perhaps even overcome this dispersive tendency to some extent. Experiments by Bond and Phillips (1990) indicated that the degree to which anion exclusion appeared to accelerate solute transport increased with decreasing water content. For reactive solute transport in a simple Na-Ca-Cl system, stochastic modeling approaches led Russo (1989a,b) to conclude that decreasing the effective saturation tended to increase retardation and reduce the spatial variability in both moisture content and hydraulic conductivity.

4.1.2.2.2.3 Bulk Density, ρ_b

If the effective porosity is less than the total porosity, use of the measured bulk density in the retardation equation (equation 1) would be inappropriate. Differences between effective and total porosity could suggest some mass of rock is inaccessible to the radionuclides. The use of bulk density in the retardation equation describes the mass of sorbing solid that interacts with the radionuclide contaminant. The maximum bulk density results from measurements of crushed material. Any adjustments to the bulk density for intact porous rock would necessarily result in smaller values.

4.1.2.2.3 CRITERION 2c. Demonstrate That the Three Implicit Assumptions (i.e., Linear Isotherm, Fast Reversible Sorption Reaction, and Constant Bulk Chemistry) Are Valid.

4.1.2.2.3.1 Linear Isotherm

To demonstrate a linear isotherm, it is necessary to determine K_d as a function of radionuclide concentration. Vermuelen and Hiester (1952) have shown that if the isotherm is linear, equation (1) can be used to calculate solute retardation. If sorbed concentration is plotted along the y-axis and dissolved concentration along the x-axis in a cartesian coordinate system, and the isotherm is nonlinear and convex up, (i.e., steep at low concentration and shallow at high concentrations), the relationship is still valid. Consequently one can predict the breakthrough curve or travel time. The only effect of this shape isotherm is that the solute front is "self-sharpening." This means the solute front has a steeper concentration gradient and longitudinal dispersion is decreased. If, on the other hand, the isotherm is nonlinear and concave up, the longitudinal dispersion is accentuated by the sorption process. In that case, equation (1) could not be used to predict retardation or breakthrough.

Some of the isotherms determined for YM (e.g., U and Cs) are nonlinear, but they are convex up. Consequently, travel time can be determined, but longitudinal dispersion is less than with a nonsorbing radionuclide.

4.1.2.2.3.2 Fast Reversible Ion Exchange and Adsorption Reactions

To demonstrate that ion exchange and adsorption reactions are fast relative to flow velocities, it is necessary to determine sorption as a function of time. It is important to demonstrate that sorption reactions are fast. Otherwise, the radionuclide can be transported faster than expected. Column experiments can be used to ascertain that the sorption reactions are fast. Column experiments studying plutonium (Thompson, 1989) indicated "a sizeable fraction of PuO_2^{2+} or PuO_2^{+} can move through crushed tuff without interaction." Batch sorption tests described in Triay, et al. (1997), indicates Pu sorption is extremely slow, not having reached a steady state in a month.

An example was provided in Comment 96 of the NRC Site Characterization Analysis (SCA) (Nuclear Regulatory Commission, 1989) that describes a hypothetical situation to be used as an abstraction for radionuclide transport and illustrates the need to identify sorption mechanisms along the flow path. In that example, there are a series of beakers that contain a nonsorptive solid. A radionuclide-bearing solution is added to the first beaker and some of the radionuclide precipitates until the system reaches equilibrium. The contents of the beaker can be analyzed and a partition coefficient can be determined describing the ratio of radionuclide on the solid to that in the liquid. The liquid from the first beaker is then decanted into the second beaker. No partitioning occurs in this beaker nor subsequent beakers, since the solution no longer exceeds the saturation limit. Consequently, no retardation occurs. A reduction in concentration takes place in the first beaker only. Application of the partition coefficient to calculate the retardation would be invalid. Column experiments involving plutonium elution indicate some reduced concentration of plutonium passes through the column at the same rate as tritium. It remains to be determined that the K_ds recommended for PA in Triay, et al. (1997) are technically defensible.

4.1.2.2.3.3 Constant Bulk Chemistry

Meijer (1990) states “a constant sorption coefficient approach is viable if the composition and physical characteristics of the flow system do not change significantly over the interval modeled in the calculations...” He goes on to say “if the composition of the system is likely to change with time, the effects of the compositional changes on the sorption coefficient must be determined for YM by either empirical and/or theoretical approaches.” Given that the new proposed rule 10 CFR Part 63 (Nuclear Regulatory Commission, 1999c) is dose based, which means radionuclide concentrations must be determined, changes in chemistry in time take on added importance. Fuentes, et al. (1987) provide an example of how a column under one set of bulk chemistry conditions can be loaded with a radionuclide. Then, with a change in chemistry, the radionuclide is stripped from the column in a wave. The concentration of the eluted radionuclide can exceed the initial concentration significantly. The concentration of the wave depends on a number of factors, including the amount of radionuclide first loaded onto the column, and the efficiency with which the radionuclide can be desorbed. Modeling 1D transport of uranium through a column, Yeh and Tripathi (1991) predicted similar conditions. In 600-day simulations using the coupled reactive transport code HYDROGEOCHEM, uranium increased above the initial feed concentration due to adsorption and desorption of surface complexes in a zone rich in iron oxyhydroxides. Introduction of a carbonate pulse during the simulation desorbed the uranium in the iron oxyhydroxide zone, leading to a secondary uranium pulse. Dispersion reduced the magnitude of the pulse but, even at the end of the simulation, the concentration at the outlet was still several orders of magnitude greater than the background uranium concentration.

Groundwater chemistry in the SZ in the vicinity of YM is subject to variability with time (Perfect, et al., 1995; Oliver and Root, 1997). It is difficult to determine whether this variability is a real reflection of natural heterogeneity or an artifact of the sampling process (well purging, sample preservation, analytical uncertainty, etc.). Similar variability has been observed for porewater samples collected from the UZ (Yang, et al., 1996a,b), but small sample volumes and uncertainty, with regard to the effect of the sampling process, also make evaluation of this variability difficult. Recent geochemical modeling by Browning, et al., (1999) has assumed equilibration of the reported porewater chemistry with observed partial pressures of CO_2 in wells UE-25 UZ#16 and USW UZ-14 (Yang, et al., 1996a,b). For UE-25 UZ#16, the model results in a much smaller range in calculated pH (8.0 to 8.6) than the reported measurements (7.0 to 9.2). Mineralogy is also variable in the YM region (Appendix A), and may exert control on both water chemistry and radionuclide transport.

4.1.2.3 CRITERION 3: Process Modeling a Approach for the Estimating Radionuclide Transport

4.1.2.3.1 CRITERION 3a. Demonstrate That a Portion of the Flow Path Acts as an Isotropic Homogeneous Porous Medium [see USFIC IRSR (Nuclear Regulatory Commission, 1998b) on Deep Percolation]

The technical basis for this criterion is the same as for Criterion 2a. (Section 4.1.2.2.1).

4.1.2.3.2 CRITERION 3b. Demonstrate That Appropriate Values for Parameters Used in Process Models Have Been Considered

4.1.2.3.2.1 Processes

Processes that can affect radionuclide transport are listed in the following table

Table 4-1. Processes affecting radionuclide transport

Transport Involving Dissolved Radionuclides	Transport Involving Radionuclides in the Colloidal or Particulate State
Surface complexation	Agglomeration/flocculation
Ion exchange	Dispersion
Precipitation/dissolution	Settling
Diffusion	Attachment
Radioactive decay	Radioactive decay
Dispersion	Filtration

Although the K_d approach to estimating radionuclide transport is simple and requires only three measured parameters (K_d, n or θ, and ρ_b), it provides no information concerning the mechanisms for radionuclide-solid interactions nor the radionuclide concentrations associated with the various liquid and solid phases. That information must come from other sources, such as solubility constraints. In comparison, process modeling can provide a mechanistic explanation for the solute-solid interactions and the radionuclide concentrations associated with the phases affecting transport conditions. However, process models generally require the determination of more parameters than for the K_d approach.

4.1.2.3.2.2 Parameters

Parameters typically used in modeling the processes listed in Table 4-1 are discussed below:

- Thermodynamic parameters that are complete, internally consistent, and have been accepted by the scientific community (e.g., Nuclear Energy Agency (NEA) Thermodynamic Database, CHEMVAL, etc.)
- Model-specific parameters such as surface complexation model (SCM) binding constants, exchange constants (ion exchange), rate constants (precipitation/dissolution) that have been determined based on accepted experimental data (QA control) or by demonstrated analogy to experimental data.
- Hydrochemical parameters including pH, PCO_2 (SCM), PO_2 (precipitation/dissolution), ionic strength (ion exchange, colloid transport), colloid concentration (colloid transport), Na^+/Ca^{2+} and Na^+/Mg^{2+} ratios (i.e., colloid transport) have been determined on site-specific groundwaters
- Mineralogic parameters constraining the solid phases that can affect radionuclide transport, including mineralogy, surface area, and mineral chemistry, have been determined for site-specific solids.
- Physical characterization of the flowpaths, including porosity, aperture, surface area, and moisture content, have been determined for site-specific materials.

The following section expands on the description of process models that affect radionuclide transport and the parameters for each process. This discussion section provides only a sample of important processes affecting radionuclide transport.

Surface Complexation

Recent work with batch experiments suggests that actinide sorption on silicate and aluminosilicate minerals is likely to be controlled by surface complexation processes (Pabalan, et al., 1997; Bertetti, et al., 1998; Turner, et al., 1998a). Hydrolysis behavior has been identified as a critical aspect of actinide sorption (Pabalan, et al., 1998; Bertetti, et al., 1998). The location of the pH-dependent sorption edges for NpO_2^+ and UO_2^{2+} are determined by the onset of hydrolysis. Because uranium hydrolysis begins at lower pH values than neptunium hydrolysis, the sorption edge of uranium is located at a lower pH. The sorption "envelope" bounded by sharp decreases in sorption at high and low pH, when expressed in terms of K_d, is sensitive to chemical parameters, such as pH and carbonate concentration, but relatively insensitive to mineral type and radionuclide concentration (Bertetti, et al., 1998; Pabalan, et al., 1998). Sorption via formation of radionuclide complexes at the mineral water interface is a principal means of sorption on oxides and oxyhydroxides of metals such as Fe, Mn, and Si, and also occurs on aluminosilicate phases, such as clays and zeolites, and on carbonates. Surface complexation models have been developed to provide a theoretical basis for modeling radionuclide sorption through surface complexation. A generalized pH-dependent sorption reaction between aqueous actinides, such as Np(V), and a variably charged surface sorption site can be represented in the form:

$$>XOH^\circ + pNpO_2^+ + nH_2O \rightleftharpoons [>XOH_q\text{-}(NpO_2)_p(OH)_n]^{p+q-n-1} + (1+n-q)H^+ \qquad (18)$$

where q is the protonation state of the sorption site (q=0, 1, or 2 for deprotonated, neutral, and protonated sites, respectively), and p and n are the reaction coefficients for NpO_2^+ and H_2O, respectively. NpO_2^+ represents the aqueous neptunyl species, and $[>XOH_q\text{-}(NpO_2)_p(OH)_n]^{p+q-n-1}$ represents the Np(V) surface complex. Similar reactions can be written for other actinides such as uranium and plutonium.

Typically, several types of parameters are required for surface complexation modeling, including

- *Model-specific binding constants*

  Binding constants for SCMs are usually determined by postulating a surface sorption reaction and adjusting the value of its equilibrium (binding) constant to match a given sorption dataset. The value of this binding constant is dependent on the SCM used, the form of the sorption reaction, and the mass action and mass balance relations in the conceptual geochemical model used in developing the SCM (Kent, et al., 1988; Davis and Kent, 1990; Turner, 1995). The experiments used to determine the binding constants should be well constrained and cover a range in minerals and conditions relevant to the site-specific conditions at YM (see technical basis for Criterion 2b).

- *Thermodynamic constants*

  The binding (equilibrium) constant for the postulated SCM surface reaction will be determined in the context of the speciation reactions that make up the chemical equilibrium model. For this reason, the binding constant is dependent on the thermodynamic data used to describe the radioelement system (Turner, 1995; Langmuir, 1997). For the radioelements of interest in the potential YM repository, examples of potential data sources include the EQ3/6 database or international efforts at standardization, such as the NEA thermodynamic database for uranium (Grenthe, et al., 1992) or americium (Silva, et al., 1995). These data should be consistent with data used in other aspects of the HLW repository program and internally consistent. Where the data are inconsistent, or where there are conflicting data from different sources, the possible effects on the sorption modeling should be evaluated. Any significant changes in the data require a recalculation of the necessary parameters.

- *pH*

  Titration experiments with oxyhydroxides and silicate minerals indicate that surface charge is a complex function of system chemistry, particularly pH (Davis and Kent, 1990; Turner, 1993). For cations, such as UO_2^{2+}, NpO_2^+, and Am^{3+}, oxyhydroxides exhibit a sharp sorption edge where, depending on radionuclide concentration and the number of available sites, sorption of cations increases from essentially zero to nearly 100 percent with increasing pH over a relatively narrow pH range; the location of the edge depends on the redox state of the element and the hydrolysis behavior of the element of interest (Dzombak and Morel, 1990; Turner, 1995; Bertetti, et al., 1998; Pabalan, et al., 1998). For anions and oxyanions such as SeO_4^{2-}, the reverse is true; sorption typically decreases in a gradual fashion with increasing pH (Davis and Kent, 1990).

- *Eh*

The oxidation state in the geologic setting may also affect sorption behavior. For example, under oxidizing conditions, technetium is principally present as pertechnetate (TcO_4^-) and does not sorb strongly, whereas, under reducing conditions, Tc^{4+} is predominant and sorbs more strongly (Lieser and Bauscher, 1988). For the actinides, sorption coefficients appear to be similar for cations of similar charge and structure. Actinides (An) with higher charges tend to sorb at lower pH values and bond more strongly (Langmuir, 1997) in the order $An^{4+} > An^{3+} > AnO_2^{2+} > AnO_2^+$. For example, for adsorption on aluminum, Th^{4+} reaches 50 percent sorption at a pH of about 2.5, Am^{3+} at about 5.5, and NpO_2^+ at about 7.5 [Bidoglio, et al. (1989)]. Some radioelements exhibit fairly simple oxidation chemistry since only one oxidation state is found in nature [e.g., Cs^+, Am^{3+} and Th^{4+}]. Other radioelements are likely to be much more complex due to the presence of multiple oxidation states [e.g., Pu(III, IV, V, VI), U(IV,VI), and Np(IV, V)].

- *Ligand concentration*

Experimental results show a link between the aqueous speciation of a radionuclide and its sorption behavior (Pabalan, et al., 1998; Bertetti, et al., 1998). For example, actinide sorption is important under conditions in which actinyl-hydroxy complexes are favored to form in the aqueous phase. Geochemical conditions that inhibit the formation of actinyl-hydroxy complexes, e.g., low pH and carbonate complex formation, suppress actinide sorption. In addition, recent experimental evidence suggests that aqueous carbonate species may compete for sorption sites (van Geen, et al., 1994). The similarity in the pH-dependence of actinide sorption on a wide variety of minerals suggest that actinide sorption is insensitive to surface charge characteristics of the sorbent as compared to the effect of changing the total number of available sites. In the presence of complexing ligands, such as CO_3^{2-}, cation sorption by a surface complexation mechanism typically decreases to zero with further increases in pH beyond the sorption maximum.

The surface charge of carbonate minerals is dominated by the balance between the dominant cation (Ca^{2+} and/or Mg^{2+}) and the carbonate anion (CO_3^{2-}). For this reason, sorption on carbonates is a complex function of pH, solution chemistry, and PCO_2. Recent efforts have focused on adapting surface complexation models to describe sorption at the carbonate/water interface (van Cappellen, et al., 1993).

Radionuclide aqueous chemistry and retardation can be affected by the presence of inorganic ligands in solution. For example, actinides tend to form strong complexes with ligands that are hard bases. For inorganic ligands common in YM groundwater, the relative strength of the actinide complexes (Lieser and Mühlenweg, 1988; Langmuir, 1997) will follow the order:

$$CO_3^{2-} > OH^- > F^-,\ HPO_4^{2-} > SO_4^{2-} > Cl^-,\ NO_3^- \qquad (19)$$

The relative strength of the complex is also dependent on the oxidation state of the actinide (Kim, 1993). For a generalized actinide An, complex strength decreases in the order:

$$An^{4+} > An^{3+} \approx AnO_2^{2+} > AnO_2^{+} \qquad (20)$$

As discussed in the preceding paragraphs, radionuclide sorption is strongly affected by pH and carbonate concentration. Ligands can affect radionuclide sorption by effectively competing with available sorption sites for the radionuclide in solution and forming complexes that do not sorb (Kohler, et al., 1996; Pabalan and Turner, 1997). For example, the addition of fluoride to the UO_2^{2+}-H_2O-Quartz system shifts the sorption edge higher by about one pH unit and produces a decrease in retardation at a given pH (Kohler, et al., 1996).

Porewater samples from the UZ have been obtained by triaxial and uniaxial compression of core samples (Yang, et al., 1988; 1996a,b; 1998). Fracture water chemistry is thought to be represented by perched water bodies (White, et al., 1980; Yang, et al., 1996b; 1998). Porewater chemistry (Yang, et al., 1996a,b) suggests that sulfate and chloride are present as ligands in UZ porewaters as opposed to the dominance of carbonate in the fractures (based on perched water chemistry). This may result in the formation of radionuclide sulfate complexes that can reduce sorption (Pabalan, et al., 1998).

The principal organic components of natural soils and waters are humic substances (Choppin, 1988; Kim, 1993), and other organics may be introduced during repository construction and operation (e.g., solvents, fuels, etc.). The anionic charge of organic molecules allows them to bind readily to cationic species in solution. For example, humic substances can complex ions in solution principally through oxygen donor sites and can bind relatively highly charged cations, such as heavy metals and actinides. In general, organic complexation of actinides is dominated by humic and fulvic acids. This can have an effect on radioelement speciation, solubility, and sorption, and may lead to the formation of radioelement colloids. Also, organic molecules may become bound as gels and coatings to the surface of inorganic particles, such as clays and oxides, changing the sorptive behavior to reflect the organic coating (Robert and Terce, 1989). For example, studies of Kohler, et al. (1992) indicate that the presence of the man-made organic ethylenediaminetetraacetic acid (EDTA) in millimolar concentrations (10^{-4} to 10^{-3} M) can significantly reduce the amount of NpO_2^+ sorbed on kaolinite. EDTA concentrations of the order 10^{-6} M, however, have only a slight effect on the sorption behavior. Triay, et al. (1997) also describes the effect of organic ligands on neptunium and plutonium sorption on iron oxyhydroxides under a limited set of pH conditions. For example, neptunium sorption on goethite, ferrihydrite, and hematite is not affected by the presence of dopamine (DOPA), but plutonium sorption on goethite and ferrihydrite is increased with the presence of DOPA. Triay, et al. (1997) attribute this to either formation of a stable surface DOPA-plutonium ternary complex, or to the reduction of plutonium from the 5+ to the more readily sorbed 4+ oxidation state. In contrast, plutonium sorption onto hematite was not significantly affected by organic compounds, perhaps due to the already high plutonium-hematite sorption (Triay, et al., 1997).

- *Surface Area*

Although the magnitude of sorption expressed in terms of K_d may differ for different mineral types, the actinide sorption behavior is similar with respect to pH dependence, and changing M/V exerts relatively little influence above a threshold value for the M/V ratio (Turner, 1995; Bertetti, et al., 1998; Pabalan, et al., 1998). This behavior is an artifact of representing sorption data in terms of K_d, which normalizes the amount of actinide sorbed to the sorbent mass and not to the number of available sorption sites on the mineral surface. In contrast, mineral specific surface area (*A*) measured by gas adsorption [e.g., N_2-Brunaues-Emmett-Telles (BET)] methods can be used as a relative measure of the number of sorption sites on the mineral surface. Further, experimental data suggest that the magnitudes of actinide sorption (at a specific pH, initial radionuclide concentration, and PCO_2) are the same for different minerals if normalized to an "effective" surface area (A′), and expressed in terms of the parameter $K_{A'}$ (mL/m^2) such that $K_{A'} = K_d/A'$ (Bertetti, et al., 1998; Pabalan, et al., 1998). For nonporous minerals such as quartz and α-alumina, A′ can be assumed equal to the N_2-BET measured surface area. For example, for minerals such as clays and zeolites, internal sites are not likely accessible for actinide sorption. Assuming A′ equal to about 10 percent of the N_2-BET measurement matches the sorption curves (expressed as $K_{A'}$) for nonporous minerals (Bertetti, et al., 1998; Pabalan, et al., 1998).

Experiments with different size fractions of crushed tuff indicate that sorption is independent of grain size down to 38 μm (Rogers and Meijer, 1993). The same study also showed that Brunauer-Emmett-Teller (BET) surface areas were also relatively insensitive to particle size. This could suggest that the particles are porous and the surface area of these internal pores greatly exceeds the external surface area of the particles.

Primary rock-forming phases in the matrix include glass, feldspar and silica polymorphs, whereas, strongly sorptive minerals, such as Fe- and Mn-oxyhydroxides, are largely limited to fractures in the YM system (Carlos, 1985, 1987, 1989; Carlos, et al., 1991, 1993, 1995a,b). Because of the relatively low specific surface areas of common matrix minerals, such as feldspar and silica polymorphs, sorption by a surface complexation mechanism may be reduced. However, given the longer residence times in the matrix, greater wetted surface area, and the presence of secondary minerals such as smectite and zeolites, surface complexation may still be an effective sorption mechanism (e.g., Bertetti, et al., 1998; Pabalan, et al., 1998).

- *Radionuclide Concentration*

  Variations in radionuclide concentrations influence transport in several ways. While sorption behavior commonly exhibits a linear relationship between solute and sorbed concentrations at low total solute concentrations, nonlinear behavior is observed with a general decrease in the slope of the sorption isotherm to near zero at higher concentrations as the saturation of the available sorption sites increases (Dzombak and Morel, 1990; Waite, et al., 1994; Pabalan and Turner, 1997). The Langmuir isotherm was developed to describe this type of behavior, assuming monolayer coverage of the mineral surface (Stumm and Morgan, 1996). An additional complication may be from the presence of more than one type of sorption site. As lower concentration, high-affinity sites are occupied, lower-affinity sites begin to dominate sorption behavior (Dzombak and Morel, 1990). Further effects on sorption behavior may be due to variations in aqueous speciation in response to changes in radionuclide concentration (Dzombak and Morel, 1990; Waite, et al., 1994; Langmuir, 1997). The radionuclide concentration relative to site coverage will ultimately determine the sorption behavior. If there is a surplus of sites (low site coverage), then a linear sorption isotherm is more likely.

- *Cation Ratios*

  In SCMs, competitive sorption includes competition among different radionuclides for available sorption sites as well as competition by common major dissolved constituents in solution such as Ca^{2+}, and Mg^{2+}. Competitive sorption experiments by Hsi (1981) suggest that Ca^{2+} and Mg^{2+} in concentrations of 10^{-3} M have relatively little effect on uranium ($\sum UO_2^{2+} = 10^{-5}$ M) sorption on Fe-oxyhydroxides. Surface complexation modeling studies (Bradbury and Baeyens, 1992; 1993), however, predicted that 10^{-6} M Ca^{2+} reduced Np ($\sum NpO_2^{+} = 2 \times 10^{-11}$ M) sorption on ferrihydrite by more than an order of magnitude at pH > 8. Increasing Ca^{2+} concentration increased the effect over a larger range in pH (pH > 7).

Ion Exchange

Minerals such as zeolites and clays exhibit a fixed charge developed by substitution of Al^{3+} for Si^{4+} in the mineral structure that is compensated by Na^+, K^+, Ca^{2+}, and Mg^{2+} in the intracrystalline exchange sites. Sorption is typically by way of ion exchange in the intracrystalline sites (Davis and Kent, 1990; Murphy and Pabalan, 1994), particularly for the alkaline and alkaline earth elements, such as Cs^+ and Sr^{2+}. Secondary matrix minerals, such as zeolite and smectite, are expected to provide a significant barrier to radionuclide transport (U.S. Department of Energy, 1988).

Typically, several types of parameters are required for ion exchange modeling, including:

- *Model-Specific exchange constants*

  Exchange constants for ion exchange models are usually determined by assuming an exchange reaction and adjusting the value of its equilibrium (exchange) constant to match a given data set. The value of this constant is dependent on the convention adopted in the ion exchange model used (e.g., Vanselow, Gapon, Gaines-Thomas), and the mass action and mass balance relations in the conceptual geochemical model used in developing the model (Langmuir, 1997; Stumm and Morgan, 1996). The experiments used to determine the binding constants should be well constrained and cover a range in minerals and solution conditions relevant to the site-specific conditions at YM (see technical basis for Criterion 2b).

- *Thermodynamic constants*

The binding (equilibrium) constant for the postulated ion exchange surface reaction will be determined in the context of the speciation reactions that make up the chemical equilibrium model. For this reason, the exchange constant is dependent on the thermodynamic data used to describe the radioelement system. For the radioelements of interest in the YM repository, examples of potential data sources include the EQ3/6 database or international efforts at standardization such as the NEA thermodynamic database for uranium (Grenthe, et al., 1992) or americium (Silva, et al., 1995). These data should be consistent with data used in other aspects of the HLW repository program and internally consistent. Any significant changes in the data require a recalculation of the necessary parameters.

- *Cation (Anion) Exchange Capacity*

For ion exchange models, the ability of a mineral to sorb through an ion exchange mechanism is commonly expressed as the cation exchange capacity (CEC) for minerals with a net negative charge, or anion exchange capacity (AEC) for minerals with a net positive charge (Langmuir, 1997). Units for the CEC/AEC are typically milliequivalents/100 g solid. The CEC/AEC also includes pH-dependent charge sites. For this reason, the CEC may exhibit a decrease with decreasing pH as H^+ competes more effectively with metal (and radionuclide) cations (Langmuir, 1997). This effect is most important for clays, and is much less important for framework silicates such as zeolites.

Clays and zeolites occur at YM as secondary replacement products. Because of interlayer exchange sites and the large surface area resulting from their layered structure, clays can have a high cation exchange capacity. Smectite, vermiculite, and some kaolinite group clays expand upon interaction with water or organic fluids. This can change the interlayer spacing, and affect the degree to which radionuclides can penetrate the interlayer ion exchange sites and sorb onto clays (Goldberg, et al., 1991).

- *Ionic Strength*

Higher ionic strength solutions in porewater relative to fractures may limit radionuclide sorption through ion exchange in the matrix (Turner, et al., 1996; Pabalan and Turner, 1997) through competition. For example, in laboratory experiments, ionic strengths on the order of 0.1 M tend to suppress ion exchange through filling of available sites by common ions such as Na^+ and Ca^{2+}. Increasing ionic strengths can also reduce interlayer spacing in clays through osmotic pressure differences, limiting access to planar exchange sites and reducing radionuclide sorption. Higher ionic strengths can also decrease the selectivity for higher valence ions. Despite the higher ionic strength in the matrix porewater relative to fracture waters, the longer residence times in the matrix, a potentially greater wetted surface area, and a greater concentration of strong sorbers such as zeolites and clays suggest that ion exchange is likely to be an effective sorption mechanism. Ionic strength values used in ion exchange modeling should be consistent with site-specific conditions anticipated at YM.

- *Cation Ratio/Concentration*

  Depending on the selectivity of the exchange sites for a given element, the concentration of common groundwater ions such as Mg^{2+}, Ca^{2+}, and Na^{+} may affect radionuclide sorption and selectivity processes through ion exchange. Generally, higher valence cations will be preferentially incorporated through an exchange mechanism (Stumm and Morgan, 1996). Higher concentrations of these elements may, therefore, reduce radionuclide sorption. The ratio of monovalent and bivalent cations may also affect interlayer swelling in clays. For example, because fewer high-valence ions are necessary to balance the negative charge at the mineral surface, the osmotic pressure is less, and interlayer swelling decreases with increasing valence of the counterions (Stumm and Morgan, 1996).

  Actinide sorption on clays and zeolites demonstrates behavior typical of surface complexation, but at low pH and low ionic strength, sorption is likely to occur by an ion exchange mechanism (Turner, et al., 1996; Pabalan and Turner, 1997; Turner, et al., 1998a). At higher pH, actinide speciation, particularly hydrolysis, tends to result in complexes that are too large to fit in the exchange structures.

Precipitation/Dissolution

One mechanism for removing radionuclides from solution is the precipitation of stoichiometric radioelement compounds or coprecipitation as impurities in other minerals. Changes in system chemistry parameters such as Eh, pH, temperature, and component concentration influence the solubility of radionuclide-bearing minerals. For example, secondary uranium silicates control uranium solubility, and may also sequester other radionuclides such as Np and Pu through coprecipitation (Murphy and Prikryl, 1996; Buck, et al., 1998). Uncertainties in thermodynamic and kinetic properties, and variable mineral stoichiometry, make realistic modeling of precipitation and dissolution of these mineral phases difficult.

Mineral precipitation and dissolution can also affect the retardation of radionuclide migration due to introduction and/or removal of sorptive minerals. Minerals such as zeolites, clays, oxides, and calcite can be dissolved and reprecipitated (Bish, 1993; Murphy and Pabalan, 1994; Murphy, et al., 1996), depending on temperature and fluid chemistry. For example, for the YM system, Murphy and Pabalan (1994) present a model for the dissolution of alkali feldspar and cristobalite to form an assemblage of clinoptilolite, smectite, and calcite that agrees broadly with observed mineral chemistry at YM. Murphy, et al. (1996) describe clinoptilolite-analcime equilibria and present evidence that suggests SZ groundwaters at YM are in apparent equilibrium with analcime. Changes in water chemistry or spatial heterogeneity, however, may bring analcime out of equilibrium, resulting in dissolution of a sorptive phase. Precipitation and dissolution of calcite may also exert significant control on the release of ^{14}C (Codell and Murphy, 1992). Calcite may also affect radionuclide release, both as a coprecipitating phase with alkaline earths such as ^{90}Sr, and as an apparent strongly sorbent phase for Np (Triay, et al., 1996a).

Matrix porosity may also be plugged by alteration minerals, limiting matrix diffusion. For example, near the Papoose Lake sill, precipitation of cristobalite and clinoptilolite within pores less than 1 cm from fracture walls suggests mobilization and diffusion of silica into the matrix, where it precipitated and reduced matrix porosity (Matyskiela, 1997). Although temperatures adjacent to the Papoose Lake sill were likely much higher than those anticipated in the far field at YM, the alteration does demonstrate the possible effects of secondary mineral precipitation on hydrologic properties.

Typically, several types of parameters are required for precipitation/dissolution modeling, including:

- *Thermodynamic constants*

  Thermodynamic modeling of precipitation/dissolution is conducted in the context of the speciation reactions that make up the chemical equilibrium model. For this reason, the amount of radionuclide uptake is dependent on the thermodynamic data used to describe the radioelement system. For the radioelements of interest in the YM repository, examples of potential data sources include the EQ3/6 database or international efforts at standardization, such as the NEA thermodynamic database for uranium (Grenthe, et al., 1992) or americium (Silva, et al., 1995). These data should be consistent with data used in other aspects of the HLW repository program and be internally consistent. Any significant changes in the data require a recalculation of the necessary parameters.

- *Kinetic Rate Constants*

  Under flow conditions, the flow rate may be fast relative to the reaction rate, and there may not be sufficient time for a precipitation/dissolution reaction to come to equilibrium. It is also possible that any precipitation/dissolution reactions will be irreversible. Under these conditions, it will be necessary to express the rate of reaction using some type of kinetic rate expression (Domenico and Schwarz, 1990; Stumm and Morgan, 1996). The forward and reverse rate constants for these expressions should be in units that are consistent with the order of the reaction and based on a set of well-constrained, time-series experiments. In the case of radionuclide transport away from the proposed HLW repository at YM, it is not likely that rate constants can be derived for each reaction of interest. In this case, rate constants should be selected to be conservative based on available experimental information and expert judgement as possible (see Criterion 4).

- *Solubility-Limiting Phase*

Estimates of radionuclide concentration limits in groundwater depend on the solubility-limiting phase selected for the calculation. The selection should be consistent with the likely groundwater chemical conditions, including redox, component concentrations, and pH. The calculation should also be performed with thermodynamic data for the solubility-limiting phase(s) that are consistent and accepted as discussed previously. Radionuclide concentrations may also be controlled by coprecipitation with secondary phases such as uranium mineralization, carbonates, and other silicates. Under the conditions of coprecipitation, the solid solution model should be consistent with available experimental and analog data.

- *Redox Conditions*

For redox-sensitive elements, such as the actinides, the redox conditions of the groundwater will have a strong effect on precipitation/dissolution of radioelement minerals. For example, reduction of UO_2^{2+} to U^{4+} greatly reduces uranium in solution through precipitation of reduced uranium minerals, such as uraninite (e.g., Langmuir, 1987) that have lower solubility limits. Field-scale analogs of this type of reduction-induced precipitation are found in low-temperature uranium roll-front deposits in the western United States (Langmuir, 1997), where a redox interface created by H_2S or by a zone of reducing organics and/or iron sulfides reduced UO_2^{2+} to U^{4+}. If appropriate thermodynamic data are available, an Eh-pH diagram can be constructed to describe the stability fields of radionuclide species and solid phases.

- *pH*

Aqueous speciation controls the solubility of radionuclides in solution. Many of the radionuclides of interest in HLW, particularly the actinides, are readily hydrolyzed. Hydrolysis of these radionuclides is dependent on the pH of the system, with hydrolysis being favored under higher pH conditions. The pH of hydrolysis varies with the radioelement of interest and its oxidation state. For example, hydrolysis of UO_2^{2+} initiates at a pH of about 3 to 4, depending on the total concentration of uranium (Turner, 1993). Hydrolysis of NpO_2^+ occurs at a much higher pH, starting at about 6 and increasing with pH (Bertetti, et al., 1998; Turner, et al., 1998a).

Because of its effects on aqueous speciation, pH conditions also influence the precipitation and dissolution of radionuclide-bearing phases. For example, uranium transport in fractured tuff at Peña Blanca, Chihuahua, Mexico, appears to be dominated by fracture flow and precipitation of a suite of secondary uranyl minerals that proceeds with time through hydrated uranyl oxides such as schoepite to hydrous uranyl silicates such as uranophane and soddyite (Pearcy, et al., 1995). The stability of these hydrous phases is dependent on the effects of pH in the mass action and mass balance expressions used in geochemical models. A similar paragenesis has been observed in long-term drip experiments using a synthetic groundwater water related to that from the J-13 well at YM and unirradiated UO_2 (Wronkiewicz, et al., 1992).

- *Temperature*

Temperature effects are important for both equilibrium systems and nonequilibrium systems (Stumm and Morgan, 1996). Measured water temperatures in the far field at YM vary from about 23 ° to 57 °C (Oliver and Root, 1997). In equilibrium models, the effects of temperature (T) are incorporated through modifying the equilibrium constant (K) according to the equation:

$$\ln K = -\frac{\Delta H^\circ}{RT} + \text{constant} \tag{21}$$

where ΔH° is the standard enthalpy change of reaction, R is the gas constant. In nonequilibrium reactions, the rate constant may vary as a function of temperature. For example, according to the Arrhenius equation for elementary reactions, the rate constant will vary according to the expression:

$$k = A \exp\left(-\frac{E_a}{RT}\right) \tag{22}$$

where the Arrhenius parameter A is a preexponential constant, and E_a represents the activation energy for the reaction. From this relationship, increases in temperature increase reaction rate constants and reaction rate.

- *Component/Ligand concentration*

The presence of some ligands in solution will favor the formation of secondary radionuclide-bearing solid phases. For example, under oxidizing conditions, increases in dissolved silica and other component species can stabilize uranium-bearing minerals such as soddyite and uranophane. These and other minerals will sequester not only U, but also other radionuclides, such as Np and Pu, through coprecipitation (Murphy and Prikryl, 1996; Buck, et al., 1998).

The strength of actinide complexes may also have an effect on mineral solubility. For example, the strength of actinide complexes follow the order discussed previously (see Criterion 3b, Surface Complexation Model parameters). Because of the potential effects of carbonate aqueous chemistry and the ready extent to which carbon dioxide dissolves into solution, radionuclide complexing and precipitation will also be controlled to some degree by the PCO_2 (Langmuir, 1997). For example, for pH > 5.5, UO_2^{2+} exhibits a higher solubility with increasing PCO_2. In uranium roll-front deposits, oxidized uranium is carried in solution as UO_2^{2+}-carbonate complexes (Langmuir, 1997). The stability field of $TcO_2 \cdot H_2O$ (s) is also decreased as a function of increasing pH (Langmuir, 1997). In general, PCO_2 in groundwaters in the Yucca Mountain region is above atmospheric ($10^{-3.5}$ bars) (Murphy and Pabalan, 1994; Turner, 1998).

- *Ionic Strength*

  Ionic strength directly affects precipitation/dissolution models through the activity coefficients in the mass action expressions for precipitation/dissolution reactions. The ionic strength of the solution may also change the rate constant for kinetic reactions. Activity coefficient models are well established and should be consistent for the ionic strength observed or predicted in the YM system. For example, based on the major and minor elements provided in the analyses of Perfect, et al. (1995), Turner (1998) calculated equilibrium ionic strength ranging from 4.34×10^{-4} molal in the most dilute groundwaters to about 1.3 molal for brines collected in playa deposits. Only 3 out of 460 sample analyses exceeded 0.5 molal; an activity coefficient model such as the Davies equation (Stumm and Morgan, 1996) should be sufficient for most of the water chemistries of interest.

- *Radionuclide Concentration*

  If radionuclide concentrations are high enough, saturation may be reached with respect to a mineral phase, depending on the concentration of other components and fluid chemical parameters such as pH. Changes in system chemistry parameters such as Eh, pH, temperature, and component concentration influence the solubility of radionuclide-bearing minerals. Uncertainties in thermodynamic and kinetic properties, and variable mineral stoichiometry, make realistic modeling of precipitation and dissolution of these mineral phases difficult.

Diffusion

Diffusion of radionuclides in groundwater in porous rock acts to smooth concentration gradients by the mass transfer from regions of high concentration to regions of low concentration. Diffusion also permits the transfer of radionuclides across a region of porous medium under no flow conditions. Revision 1 of the IRSR of the USFIC KTI (Nuclear Regulatory Commission, 1998b) contains an extensive discussion on matrix diffusion. Matrix diffusion is the process of diffusion of solute into the matrix from a fracture. The conceptual model involves contaminated groundwater flowing in the fracture and relatively immobile groundwater exists in the matrix. Since the process deals with fractured rock, it is not considered in this subissue, which considers only with homogeneous isotropic porous rock. The diffusion coefficient of a radionuclide relates its flux to the concentration gradient measured in the same direction. The diffusion coefficient depends on the size of the diffusing species, its charge, the tortuosity of the porous medium, the apertures of the pores, and the moisture content of the rock.

Radioactive Decay

Radioactive decay is a general term for the process by which unstable radionuclides disintegrate spontaneously to form a different nuclide that may or may not also be radioactive (Faure, 1977). Passing through a decay chain of intermediate steps, the element will eventually decay to a stable element, such as ^{206}Pb at the end of the ^{238}U series. Although this element may be toxic (such as Pb), it is not radioactive.

Typically, several types of parameters are required for radioactive decay modeling, including:

- *Inventory*

  For calculations involving the effects of radioactive decay on radionuclide transport an estimate should be made of the inventory of the different radioisotopes in the HLW at the time of repository closure. This inventory will depend on the quantities of different waste streams (e.g., spent fuel or defense waste). These quantities will depend on design decisions that have not yet been finalized. The inventory models are primarily considered as a part of the TSPAI KTI.

- *Decay Constant*

  To account for the effects of radioactive decay properly, transport models should include decay chains of the radioelements of interest with appropriate decay equations constants. The rate of change in the number (N) of atoms of a given radionuclide due to radioactive decay is governed by the expression:

$$-\frac{dN}{dt} = \lambda N \tag{23}$$

where λ is the decay constant of the radioelement of interest (in units of inverse time). The number of atoms (N) that remain from some original amount of radioelement (N_0) at a given time (t) is expressed by the equation:

$$N = N_0 e^{-\lambda t} \tag{24}$$

This can affect radionuclide transport either by reducing the amount of a radionuclide by decay, or increasing the inventory of a radionuclide through ingrowth. Radioactive decay may lead to the formation of radioelements that are more (or less) attenuated during radionuclide transport than the parent radioelements.

For some radionuclides, such as ^{99}Tc, ^{239}Pu, and ^{237}Np, the rate of decay (half-lives on the order of 10^4 to 10^6 yr) is slow relative to a regulatory time frame, and for others (such as tritium) it is relatively fast. Radioelements with long half-lives may also produce radionuclides of concern through decay. For the radioelements of interest at YM, the decay constants are known with good precision, and the inventory at a future time can be calculated in a straightforward manner.

Colloid Transport

Colloids are typically defined as suspended particles between about 1 nm and 450 nm, although particles as large as 1 µm and greater may be mobile in the subsurface (McCarthy and Zachara, 1989). Colloidal transport of radionuclides may have an effect on the time of arrival of radionuclides at the location of the critical group. For example, Travis and Nuttall (1985a) argued that colloidal transport could be used to explain the rapid migration of Am and Pu to depths of 30 m from surface storage facilities at LANL. In a field study at LANL, Penrose, et al. (1990) observed that 85 percent of ^{242}Pu tended to be associated with particles > 25 nm, while 43 percent of ^{243}Am was associated with particles < 2 nm in diameter. These actinides had migrated up to 3,000 m from the inferred point of origin, but there is some question as to whether this represented actual subsurface transport or surface runoff (Marty, et al., 1997). Recent field studies involving groundwater pumped from wells downgradient from the Benham underground detonation cavity at the NTS also suggest enhanced transport of radionuclides, such as Pu, Co, Eu, and Cs, associated with a colloidal phase (Kersting and Thompson, 1997; Smith, 1997; Thompson, 1998; Kersting, et al., 1999). For example, evidence reported in Thompson (1998) and Kersting, et al. (1999) suggests that plutonium associated with a colloidal phase has migrated to a well about 1.3 km south of the Benham event. The ^{240}Pu/^{239}Pu isotope ratio of the samples was used to establish a link between the Pu in the sampling well and Pu that originated in the Benham detonation cavity. Total Pu concentration was low (10^{-14} M), but > 99 percent of the Pu was associated with particles ranging from > 1 µm to < 7 nm in diameter (Kersting, et al., 1999).

Colloids involving radionuclides are typically called radiocolloids and have been divided into two types (Maiti, et al., 1989; McCarthy and Zachara, 1989). "True" or "real" colloids are generally formed from hydrolysis, polymerization, condensation, or precipitation of radionuclide compounds in solution. In contrast to true colloids, pseudocolloids are formed when the radioelements sorb on small particles already present in the groundwater. These particles may be either natural or introduced by human activity, and include organic and inorganic carbon, silica, clay particles, and oxyhydroxide compounds of metals, such as Fe, Mn, and Al. The presence, stability, composition, and sorptive capacity of these particles are dependent on different aspects of the chemistry of the groundwater system. Further complicating the behavior of pseudocolloids is the possibility of nonsorptive particles being coated with sorptive materials (Robert and Terce, 1989). Experimental evidence has also demonstrated that colloids can be formed as secondary alteration products, such as clays, and released from HLW forms (Bates, et al., 1992; 1995; Ebert and Bates, 1992; Finn, et al., 1994).

Typically, several types of parameters are required for colloid transport modeling, including:

- *Particle Concentration*

  The total concentration of colloid-sized particles will affect the total amount of radionuclide that may be associated with a colloidal phase. Since there is no flowing water at the proposed repository site, well J-13 in Jackass Flats to the east of YM was sampled for natural colloids (Kerrisk, 1987; U.S. Department of Energy, 1988). Filtering of 9,300 L of water through the membrane filters yielded about 2.7 × 10^{-5} g/L of particulate material. The bulk of the material was retained by the 400-nm filter assemblies, and the 5–400 nm filtrate accounted for less than 1 percent of the total yield. Based on these analyses, there seems to be at least some natural colloidal matter suitable for the formation of pseudocolloids.

Buddemeier and Hunt (1988) studied colloidal transport in hydrologically saturated fractured tuff and lava rock at the site of the Cheshire event on the NTS. Water samples were filtered from 3 nm to 1 μm. Essentially all of the transition (Mn, Co) and lanthanide (Ce, Eu) radioelements were associated with the colloidal fraction retained by filtration and found at distances up to 300 m downgradient from the detonation cavity. For the 3 to 50 nm size fraction, colloid mass concentration in the formation was about 4.5 mg/L. Although this is higher than the J-13 waters, Buddemeier and Hunt (1988) report relatively high pumping rates (~120 L/min), raising the possibility of increased suspension of particulates due to hydrodynamic shear forces. In the detonation cavity, colloid concentration was higher, ranging from 10.1 (3–50 nm) to 63 (6–450 nm) mg/L. XRD studies on one sample from the detonation cavity indicated that the bulk of the 3–50 nm retentate was dominated by quartz, and (Ca, K) feldspars, with a possible clay fraction of about 10 percent. Buddemeier and Hunt (1988) also report that the groundwaters in the Pahute Mesa drainage in the northern part of the NTS contain 0.8–6.9 mg/L particles > 30 nm, and one spring on the NTS contains about 16.4 mg/L particles in the 30–400 nm size fraction.

Kingston and Whitbeck (1991) collected and analyzed 23 groundwater samples from central and southern Nevada, including springs and wells in Quaternary alluvium in the Amargosa Desert and on the NTS (e.g., Lathrop Wells, Fairbanks Spring, Ash Springs, Crystal Pool, Cane Springs). Size fractions from 30 nm to larger than 1 μm were examined. Most of the water samples contained less than 1 mg/L of colloidal sized particles, but concentrations of up to 145.8 mg/L were reported in one sample.

- *Particle Mineralogy*

Particle mineralogy will determine the extent to which a mineral may act as a platform for radionuclide sorption and pseudocolloid formation. Analysis of the 400-nm to 10-μm fraction from J-13 with scanning electron microscopy (SEM) and emission spectroscopy indicated a composition dominated by Si-Fe-Ca, with minor Al, while the 5–400 nm fraction was predominantly Na-Si with minor amounts of Ca and Fe (Kerrisk, 1987; U.S. Department of Energy, 1988). Equilibrium speciation calculations performed with the MINTEQA2 code (Allison, et al., 1991) for the J-13 well water in contact with atmosphere, indicate that, although J-13 water is undersaturated with respect to calcite, groundwater is supersaturated with respect to ferrihydrite, kaolinite, montmorillonite, and several other minerals that may form coatings or natural colloids favorable to the formation of pseudocolloids.

In addition to natural colloids already present in the YM environment, the construction, operation, and permanent closure of the repository may introduce additional material. These sources can include corrosion of the canisters and glass wasteforms (Bates, et al., 1992, 1995; Ebert and Bates, 1992; Finn, et al., 1994), degradation of backfill materials, such as clays (Travis and Nuttall, 1985b; Salbu, et al., 1987), drilling muds, and the introduction of organic materials, such as EDTA, during the processing of the waste (Means, et al., 1978a,b; Means and Wijayaratne, 1982) and construction of the repository.

- *Ionic Strength*

If actinides and other radioelements can sorb onto pseudocolloids or form true colloids, the stability of the particles in suspension is of critical importance to colloid-mediated transport. At low ionic strengths, the electrostatic double layer (EDL) expands outward from particle surfaces, stabilizing the colloids in solution through electrostatic repulsion. At higher ionic strengths, the double layer collapses, and the charged particles begin to flocculate (agglomerate) and come out of suspension, due to gravity settling and filtration. An additional possibility is that a decrease in the solution ionic strength may extend the EDL, leading to a release of attached particles (Kallay, et al., 1987). Kallay, et al. (1987) also indicate that sweeping the resuspended particle away from the surface is necessary to prevent reattachment. Variations in overall solution chemistry (pH, component concentrations) and moisture content of the medium influence the magnitude of the ionic strength effects.

Based on observed colloid particle concentrations and groundwater ionic strength for field sites in a variety of rock/water systems throughout the world, TSPA-VA (Civilian Radioactive Waste Management System, Management & Operating Contractor, 1998a, Section 4.4.3.3.1) presented an empirical relationship between colloid particle concentration (particles/mL) and ionic strength (molal), expressed as:

$$\log[\text{coll}]\ (\text{particles/mL}) = 7.0 - 34 \times I.S.\ (\text{molal}) \qquad (25)$$

There is still a relatively large uncertainty remaining in this empirical relationship (Civilian Radioactive Waste Management System, Management & Operating Contractor, 1998a, Section 4.4.3.3.1).

- *pH*

Groundwater pH may have an effect on colloid stability by controlling surface charge on variably charged minerals, such as oxyhydroxides (Stumm and Morgan, 1996). For pH conditions near the point-of-zero-charge (pH_{ZPC}) for a given mineral, surface charge is small. As the groundwater pH diverges from the pH_{ZPC}, the surface charge increases. Depending on the mineral, the increased charge may lead to electrostatic attraction between positively charged oxyhydroxides and aluminosilicates that exhibit a permanent negative due to Al^{3+} substitution for Si^{4+}. This agglomeration destabilizes the suspension and decreases colloid transport.

Groundwater pH may have an effect on the possibility of forming true radiocolloids. Several of the radionuclides predicted to be important in repository performance (Kerrisk, 1985) are known to form true radiocolloids through hydrolysis, polymerization, and crystallization (Patera, et al., 1990). True colloid stabilization is favored under alkaline conditions, especially in the case of highly charged, redox-sensitive species such as actinides (Maiti, et al., 1989; Choppin and Mathur, 1991). Both Am and Pu exhibited appreciable colloidal formation at high pH, possibly as $Am(OH)_3$ and $Pu(OH)_4$, respectively (Olofsson, et al., 1982a,b; 1985). In contrast, Np colloid formation was negligible, except at pH > 10 for high ionic strength solutions (1 M $NaClO_4$). Hobart, et al. (1989) reported on the preparation and analysis of Pu(IV) colloidal sols, and observed that the redox potentials of the colloids differed significantly from those predicted for dissolved Pu^{+4} ions. Using autocorrelation photon spectroscopy, Rundberg, et al. (1988) determined that the diameter and density of ^{242}Pu colloids were 2.9±0.2 nm and 9.0 g/cm^3, respectively. Rundberg, et al. (1988) also observed that a ^{239}Pu colloid formed in the experiment remained stable at a particle size of 180 nm for over 2 yr.

Groundwater pH is also a key parameter for determining radionuclide sorption on pseudocolloids, with effects as discussed previously in Criterion 3b, surface complexation modeling.

- *Redox Conditions*

Olofsson, et al. (1982a,b) indicated that the formation of colloids is favored for the actinides in lower (+3, +4) valence states. Am and Pu are examples of radionuclides that tend to form stable colloids (Kim, 1993). It is expected that oxidizing conditions will dominate the YM system, but there may be localized reducing areas that could have an effect on colloid formation and transport.

- *Ligand concentration*

The presence of inorganic ligands such as HCO_3^- and SO_4^{2-} and CO_3^{2-} can affect the formation of pseudocolloids by reducing radionuclide sorption (see Criterion 3b—Surface Complexation Model parameters). Particle interaction with dissolved ligands may also serve to reduce or even reverse surface charge (van Geen, et al., 1994; Stumm and Morgan, 1996). The higher the concentration of these ligands, the more pronounced desorption from the pseudocolloid may become. The concentration of organic ligands may have an effect on the formation of pseudocolloids by providing a sorptive coating on existing groundwater colloids or forming sufficiently large organo-metallic compounds that act as colloid-sized particles. For example, in an oligotrophic lake in Wales, Orlandini, et al. (1990) observed that over 80 percent of the actinides Am, Th, and Pu were associated with organic compounds >450 nm. Kim, et al. (1987) also proposed the generation of centrifugable Am true radiocolloids in experiments performed with natural groundwaters containing significant amounts of dissolved organic carbon (DOC).

Organic material is reported in J-13 well water (Means, et al., 1983; U.S. Department of Energy, 1988). Total organic carbon is reported at 0.14±0.05 mg/L, and compounds greater than 1,000 g/mol make up more than 50 percent of the material. In addition to naturally occurring organic components, human activity associated with a HLW repository may also introduce colloidal materials in the form of organics associated with waste treatment, dissolution of vitrified waste-forms, and organic matter used in drilling, construction, and repository operations (Travis and Nuttall, 1985b).

- *Porosity/Aperture and Particle Diameter*

The effectiveness of colloids in enhancing (or retarding) radionuclide migration is dependent on the efficiency with which these particles are transported through the groundwater system. Colloid migration may be enhanced relative to fluid flow due to volume exclusion effects and reduced particle/medium interaction. Conversely, colloids may be retarded through various physical and chemical filtration mechanisms resulting from interaction between the different phases of the colloid-rock-water system.

McDowell-Boyer, et al. (1986) divided filtration processes into three basic classes: surface (cake) filtration, straining, and physical-chemical filtration. Surface filtration involves building a barrier at the water/pore interface. This type of filtration occurs when the particles are too large to enter the pores of the medium. Even if the particles are small enough to enter the porous medium, the tortuous path they must follow may eventually lead to a constriction that is too small for them to pass through. This leads to a straining of the colloids from solution.

Particles may be removed from suspension by interaction with the pore walls, either through physical processes, such as Brownian diffusion, gravitational sedimentation, or through chemical processes, such as sorption due to electrostatic attraction. Once particles have been deposited, there is a possibility that they may be resuspended. The distances calculated for the energy attachment well (0.3–1 nm) are generally smaller than the diameter of the particle. While London-van der Walls forces generally predominate at these ranges, energy provided from Born repulsive forces, or thermal and hydrodynamic energy, can overcome the attraction energy well and lead to particle erosion and re-entrainment.

Although the size of colloids makes them vulnerable to several different filtration mechanisms, it is also possible that particle size (Bales, et al., 1989) will lead to volume exclusion and a less tortuous, more rapid path to the accessible environment. In pores and fractures, the water velocity distribution is such that the maximum velocity is along the centerline of the fracture, while minimum velocity occurs at the fracture wall. Because of their size, colloids can never "experience" the minimum water velocity and, as such, the average colloid velocity will be greater than that of the water. In general, this effect, called hydrodynamic chromatography (de Marsily, 1986), becomes more pronounced with increasing particle diameter. In addition, electrostatic repulsion associated with charged particles will tend to keep the particles away from the surfaces, further enhancing the effect. Since the particle charge is a function of pH and ionic strength, hydrodynamic chromatography in a natural environment varies as a function of solution chemistry (de Marsily, 1986).

Colloid transport in the matrix at YM may be limited, due to the small size of the available porosity. Physical filtration is likely to provide a first barrier to colloid transport through the matrix. Mercury porosimetry data (Travis and Nuttall, 1987) shows that most of the pores in the Topopah Spring tuff matrix have an aperture of less than 1.0 μm, and more than 50 percent of the pores have apertures less than 0.1 μm. Porosity is even smaller in the Calico Hills formation, with 50 percent of the pores less than 0.06 μm in diameter, although there are pores up to 4 μm in diameter (Travis and Nuttall, 1987). Chemical filtration through attachment to pore walls is likely to provide an additional barrier to colloid transport through the matrix. Tracer tests at the C-Well complex (UE-25 c#1, c#2, and c#3) indicate that colloid-sized particles (0.36 μm diameter polystyrene microspheres) migrated 31.7 m through the Lower Bullfrog tuff, but were attenuated by filtration, with only about 11 percent recovery after 2,650 hr (Reimus and Turin, 1997). It is much more likely that if colloid transport of radionuclide occurs at YM, it will be limited to fractures. Fracture transport processes, including colloid transport, will be considered in more detail under Section 4.3.

4.1.2.3.3 CRITERION 3c. Demonstrate That the Three Implicit Assumptions (as in 2c) Are Valid, If Process Models Are Intended to Yield a Constant K_d for Use in the Retardation Equation (Equation 1); Otherwise, Determine Transport in a Dynamic Reactive Transport System Model (e.g., PHREEQC, MULTIFLO, HYDROGEOCHEM, etc.)

The constant K_d approach models only the retardation of the radionuclides, (i.e., the ratio of the velocity of groundwater to the velocity of the radionuclide). This approach does not consider the concentration of radionuclide in the contaminant plume. However, process models can be used to calculate radionuclide concentration. Radionuclide concentrations are assumed to be controlled by solubility constraints or leach limits of the source term. For those radionuclides with low solubilities, the concentration is often conservatively assumed to be at the radionuclides solubility limit. For radionuclides with high solubilities, on the other hand, the control of the radionuclide concentration is frequently assumed to be leach limited, meaning some percent of the inventory per year is available for release. The radionuclide concentration then is assumed to remain constant all along the flowpath from the source to the biosphere. Recent PA have begun to take credit for dilution caused by the assumed mixing at the water table of the limited volume of contaminated recharge with the large volume of uncontaminated groundwater that passes under the repository in the SZ. Also, dilution has been considered in the portion of the aquifer affected by pumping the well. The contaminated stream tube is combined with noncontaminated streamtubes to yield a water with diluted radionuclide contamination.

Process models can also be used to demonstrate the three assumptions explicit in the appropriate application of K_d values to determine retardation. Process modeling can also indicate whether multiple radionuclide species are expected. Evaluation of the rates of reactions between dissolved species and adsorbent would be needed to ascertain whether different species of the same element could migrate at different rates.

If the assumptions cannot be demonstrated to be valid, then coupled flow and transport modeling should be used to estimate radionuclide transport and the concentration of radionuclides in the groundwater and on the solids. Yeh and Tripathi (1991) describe hypothetical cases where the variability of the bulk chemistry along flow paths causes excursions in the radionuclide concentrations. Furthermore, the K_d values at fixed locations along the flowpath may change significantly over time as a result of the change in chemistry.

4.1.2.4 CRITERION 4: Where Data Are Not Reasonably or Practicably Obtained, Expert Judgement Has Been Used and Expert Elicitation Procedures Have Been Adequately Documented. If Used, Expert Elicitations Were Conducted and Documented in Accordance with the Guidance in NUREG-1563 (Nuclear Regulatory Commission, 1996) or Other Acceptable Approaches. Expert Elicitation and Sensitivity Analyses Should Not Be Used as a Replacement for Experimental and Field Data, Where Such Data Can Be Reasonably Obtained.

As summarized in Nuclear Regulatory Commission (1996), the NRC expects that subjective judgements of groups of experts will be used by DOE to assess issues related to overall performance of the proposed HLW repository at YM. The NRC has traditionally accepted expert judgement as part of a LA to supplement other sources of scientific and technical data. Expert elicitation is commonly used when:

- Empirical data are not reasonably obtainable or analyses are not practical to perform
- Uncertainties are large and significant to a demonstration of compliance
- More than one conceptual model can explain, and be consistent with, the available data
- Technical judgements are required to assess whether bounding assumptions or calculations are appropriately conservative

Nuclear Regulatory Commission (1996) also summarized a series of technical positions and procedures concerning the use of expert elicitation in demonstrating compliance with geologic repository disposal regulations. These procedures emphasize the need for detailed documentation during the elicitation and for transparency in the aggregation of multiple experts' judgements. An elicitation also should provide a means to evaluate new data that may arise between completion of the elicitation and submittal of licensing documents (Nuclear Regulatory Commission, 1996).

Expert elicitations have been used in previous PAs to supply distributions of K_d values. Sorption coefficients for some radionuclides have been determined using site-specific materials. These radionuclides include americium, uranium, neptunium, plutonium, strontium, cesium, selenium, tin, nickel, technetium, cerium, europium, and barium (an analogue for radium). Sorption parameters for other radionuclides were estimated by expert elicitation using nonsite-specific analogue data. These radionuclides include thorium, protactinium, lead, actinium, samarium, niobium, and zirconium (Triay, et al., 1997).

4.1.2.5 CRITERION 5: Data and Models Have Been Collected, Developed and Documented under Acceptable QA Procedures (e.g., Altman, et al., 1988), or If Data Were Not Collected under an Established QA Program, They Have Been Qualified under Appropriate QA Procedures.

Both DOE and NRC have approved QA programs for technical investigations conducted by their respective agencies and contractors, and the NRC has stated that the quality of data will be acceptable if the data are developed under an approved QA program. These QA programs detail the procedure necessary to collect, document, and develop data and models in an acceptable manner. Periodic technical audits are conducted by the DOE and the NRC to ensure that appropriate QA procedures are implemented in technical investigations. These audits are usually attended by observers from each agency, who provide an independent assessment of audit effectiveness and conclusions.

4.2 RADIONUCLIDE TRANSPORT THROUGH ALLUVIUM

4.2.1 Review Methods and Acceptance Criteria

The DOE considers radionuclide transport a key performance attribute of the natural barrier system in the proposed repository. Retardation of radionuclides through alluvium constitutes a key element of the NRC subsystem abstraction for PA. The DOE must adequately estimate the transport characteristics of the YM site and appropriately consider radionuclide transport through the alluvium in their assessments of repository performance. The review process should determine which transport processes have been addressed/assumed by DOE. The reviewer should identify first, if the selected retardation processes are appropriate to the YM system, and second, whether they are addressed adequately for those radionuclides of concern.

Because alluvium is typically modeled as a porous medium (Nuclear Regulatory Commission, 1999a; U.S. Department of Energy, 1998c), the following *Acceptance Criteria*, which are the same as those for radionuclide transport through porous rock, apply to evaluating the DOE estimates and consideration of radionuclide transport through the alluvium:

1. For the estimation of radionuclide transport through alluvium, DOE has

    a. Determined, through PA calculations, whether radionuclide attenuation processes such as sorption, precipitation, radioactive decay, and colloidal filtration are important to performance

    b. (i) Assumed K_d is zero and radionuclides travel at the rate of groundwater flow, if it has been found that radionuclide attenuation is unimportant to performance, and it can be demonstrated that this assumption is conservative in which case, Acceptance Criteria 2 and 3 do not have to be met; or, (ii) demonstrated that Criterion 2 or 3 has been met, if radionuclide attenuation in alluvium is important to performance or if an assumption that K_d is zero in alluvium is not conservative..

2. For the valid application of the K_d approach, using equation (1) $R_f = 1 + \rho_b K_d/n$, DOE has

    a. Demonstrated that the flow path acts as an isotropic homogeneous porous medium (see USFIC IRSR (Nuclear Regulatory Commission, 1998b), deep percolation on subissue describing methods of estimating matrix properties as parameters.)

    b. Demonstrated that appropriate values for the parameters, K_d, n or θ, and ρ_b have been adequately considered (e.g., experimentally determined or measured)

c. Demonstrated that the three implicit assumptions (i.e., linear isotherm, fast reversible sorption reaction, and constant bulk chemistry) are valid.

3. For the valid application of process models such as surface complexation, ion exchange, precipitation/dissolution, and processes involving colloidal material, DOE has

   a. Demonstrated that the flow path acts as an isotropic homogeneous porous medium (see USFIC IRSR (Nuclear Regulatory Commission, 1998b), deep percolation on subissue describing methods of estimating matrix properties as parameters.)

   b. Demonstrated that appropriate values are used in processes models

   c. Demonstrated that the three implicit assumptions (as in 2c) are valid, if process models are intended to yield a constant K_d for use in equation (1); otherwise, determined transport in dynamic reactive transport system model (e.g., PHREEQC, MULTIFLO, HYDROGEOCHEM, etc.)

4. Where data are not reasonably or practicably obtained, expert judgement has been used and expert elicitation procedures have been adequately documented. If used, expert elicitations were conducted and documented in accordance with the guidance in NUREG-1563 (Nuclear Regulatory Commission, 1996) or other acceptable approaches. It is important to remember that expert elicitation and sensitivity analyses are not to be used as a replacement for experimental and field data, where such data can be reasonably obtained.

5. Data and models have been collected, developed, and documented under acceptable QA procedures (e.g., Altman, et al., 1988), or if data were not collected under an established QA program, they have been qualified under appropriate QA procedures.

4.2.2 Technical Bases for Acceptance Criteria

It is important to note that most, if not all, of the processes and parameters/properties that affect alluvial radionuclide transport are expected to be the same as those identified in Section 4.1.2 for radionuclide transport through porous rock. The magnitude of the process or effect may be different, however, due to differences in the chemical and hydrological system in alluvium as compared to matrix. For example, sorption through a surface complexation mechanism will operate in the same fashion in both the alluvium and the porous rock, but differences in the water chemistry and mineral chemistry (see Section 4.1.2.) will control the extent to which sorption occurs by this mechanism. The technical bases for the acceptance criteria for radionuclide transport through alluvium are the same as those described in Section 4.1.2. To avoid duplication, the discussion of the technical bases presented in the next section will be limited to differences that are to be expected given likely variations between the alluvium flow system and the rock matrix flow system. Available information on mineral chemistry of tuffaceous porous and fractured rocks are well documented (Carlos, 1985; 1987; 1989; Carlos, et al., 1991; 1993, 1995a,b; Vaniman, et al., 1996a), but data for alluvium mineralogy

(Claassen, 1985) is very limited, as is water chemistry along the flowpath in the alluvium (White, et al., 1980).

The following section expands on the description of process models that affect radionuclide transport and the parameters required for each process. This discussion section is not intended to be exhaustive, and provides only a sample of important processes affecting radionuclide transport.

4.2.2.1 Processes Affecting Radionuclide Transport through the Alluvium

4.2.2.1.1 Surface Complexation

Surface complexation processes in transmissive zones and aquifers in the alluvium will operate in the same way as in the porous rock of the tuff aquifers. The degree to which surface complexation is effective in the alluvium will, therefore, be dependent on the mineralogy and chemistry of the alluvial flow system. Because there is not much information available on the mineralogy of the alluvium in the YM vicinity, it is difficult to predict the sorptive behavior radionuclides in the alluvial aquifers. Minerals in the alluvium typically reflect the mineralogy of the local bedrock (Claassen, 1985). Zeolitized and altered tuff units are not durable, however, and much of the alluvium may be made up of resistant primary minerals such as silica polymorphs that are less sorptive due to relatively low surface areas (Bertetti, et al., 1998; Pabalan, et al., 1998). Secondary sorptive minerals such as clay deposits may form in the near surface, but it is not clear if these are present at depth. Fracture mineralogy of indurated alluvium will be dominated in the near surface by calcite and caliche formed by infiltrating fluids, although Mn- and Fe-oxyhydroxides are observed (Nye County, 1999).

4.2.2.1.2 Ion Exchange

Ion exchange processes will operate in the alluvial aquifers in the same manner as that described in Section 4.1.2 for radionuclide transport through porous rock. Secondary alluvial minerals such as clays and zeolites may provide ion exchange sites to serve as a barrier to radionuclide transport through the alluvial aquifers. Higher ionic strength solutions in alluvial waters relative to rock fracture water may limit radionuclide sorption through ion exchange in the alluvium (Turner, et al., 1996; Pabalan and Turner, 1997), but again, given the longer residence times in the alluvium, a greater wetted surface area, and a greater concentration of strong sorbers such as zeolites and clays, ion exchange is likely to be an effective sorption mechanism.

4.2.2.1.3 Precipitation/Dissolution

Precipitation/dissolution mechanisms in the alluvium and their effect on radionuclide transport will be similar to those in the porous rock system, but differences in solution chemistry may lead to different minerals and different degrees of mineralization. Because of the distance from the source (kilometers), radionuclide concentrations are likely to be below saturation with pure radionuclide phases, but coprecipitation with secondary minerals remains a possibility.

4.2.2.1.4 Dispersion

Over the longer flow distances in the alluvial aquifer system, dispersion may be an important mechanism for reducing radionuclide concentration in the groundwater. At the 5 to 20 km distances being considered in PA, however, the likely shape of a contaminant plume is poorly understood, particularly with regard to vertical dispersion (Fedors and Wittmeyer, 1998). Generally, longitudinal and horizontal dispersivity are considered to be scale-dependent (Gelhar, et al., 1992) with a longitudinal/horizontal ratio of 10. For transport in the range of up to 10 km, vertical dispersivity is reported to be less than 1 m (Gelhar, et al., 1992). The DOE TSPA-95 (TRW Environmental Safety Systems, Inc., 1995) assumed longitudinal dispersivity in the SZ equal to 10 percent of the path length from the proposed repository to the accessible environment (e.g., 500 m for a 5 km distance). Since the RIP code used in TSPA-95 is a 1D code, no vertical dispersion was considered.

Neglecting the effects of radioactive decay and sorption, Fedors and Wittmeyer (1998) provide an analysis of 3D dispersion of a contaminant plume using dispersivities in the ratio of 20/2, 50/5, and 100/10 for longitudinal and transverse directions. Vertical dispersivities ranged from 0.1 to 2, and were generally chosen to be an order of magnitude less than the horizontal dispersivity. Contaminant concentration at the centerline of the plume was reduced by a factor of up to 80 at 25 km, with dilution increasing with increasing dispersivities.

The effectiveness of dispersion depends on the conditions of the release of the radionuclide. If there is a large inventory of a radionuclide with low solubility, the concentration of radionuclide at the biosphere will approach a steady state, given enough time. Dispersion will have its greatest influence only on the contaminant front, spreading and decreasing the concentration gradient. If, on the other hand, the inventory is low, and the radionuclide solubility is high, the release can be better approximated as a pulse. Under these circumstances, without the continuous source of radionuclide to replenish the peak, dispersion could effectively reduce radionuclide concentration.

Dispersion and mixing at the well bore are transport mechanisms that will be further investigated in detail as part of the USFIC KTI (Nuclear Regulatory Commission, 1998b). Concentration of radionuclides through evaporation and plant uptake at discharge points is also a possible scenario (Carter and Pigford, 1998), although significant uncertainty remains.

4.2.2.1.5 Radioactive Decay

Radioactive decay (see Section 4.1.2.) will occur in the same manner in both the alluvium and the tuff aquifer flow systems.

4.2.2.1.6 Matrix Diffusion

Matrix diffusion may occur in the alluvial aquifer, but there is insufficient information to provide site-specific constraints on its extent. The physical characteristics of flow system of the alluvium are poorly known. If the alluvium can be envisioned as a large homogeneous, isotropic sandbox, modeling of radionuclide transport is relatively simple. If, on the other hand, the alluvium is envisioned as a complex network of buried braided streams, the possibility of preferential pathways would have to be considered. Consequently, processes like matrix diffusion, which depend on portions of the medium that contain mobile water and portions that contain immobile water, may occur in the alluvium. The USFIC KTI is addressing the issue of matrix diffusion along the flowpath, including the alluvium (Nuclear Regulatory Commission, 1998b).

4.2.2.1.7 Colloid Transport

Colloid formation, stability, and transport through a porous medium are governed by the same principles discussed earlier. There is evidence for colloid transport through the aquifer system. Kingston and Whitbeck, (1991) collected and analyzed 23 groundwater samples from central and southern Nevada, including springs and wells in Quaternary alluvium in the Amargosa Desert and on the NTS (e.g., Lathrop Wells, Fairbanks Spring, Ash Springs, Crystal Pool, Cane Springs). Size fractions from 30 nm to larger than 1 µm were examined. Trends were not observed relating colloid concentration or composition with groundwater chemistry. Inorganic colloids were predominantly silica, clay, zeolites and some calcite. Pu, Cs, Co, and Eu all sorbed to colloids collected at the NTS, and Pu and Eu may sorb preferentially on colloids rather than the immobile aquifer materials (Thompson, 1998; Kersting, et al., 1999).

4.2.2.2 Parameters/Properties Affecting Radionuclide Transport Processes Through the Alluvium

4.2.2.2.1 Alluvium Mineralogy

Alluvium mineralogy is not well constrained in the YM vicinity. Valley fill mineralogy typically is believed to be similar to the nearby bedrock outcrops in the watershed, depending on the degree and orientation of the valley slope (Claassen, 1985). A map of surface distribution of valley fill material is provided in Claassen (1985). In general, most of the alluvium near YM and north of the Amargosa Desert is made up of tuff and tuff detritus from the surrounding volcanic highlands and has a mineralogy similar to the original tuffs. Areas near YM dominated by tuffaceous alluvium include Fortymile Canyon, and the drainages from Fortymile Canyon into the Amargosa Desert. Near YM, alluvium includes material from the tuff units at the site, and is mostly limited to the more durable welded units of the Tiva Canyon and Paintbrush Tuffs (Claassen, 1985). East of Fortymile Canyon, the alluvium contains rhyolite from the Calico Hills and the upper reaches of Fortymile Canyon. Alluvium in the Amargosa Desert is identified as mixed lithology and is made up of detritus from Paleozoic carbonate and clastic rocks, as well as from the Tertiary volcanics. The southern and eastern borders of the Amargosa Desert tend to be dominated by carbonate rock clasts due to erosion from the Funeral Mountains to the south, and the Striped Hills, Skull Mountain, and the Spring Mountains to the east (Claassen, 1985).

Size fractions range from clay in the basin centers to cobbles and boulders closer to outcrop (Cornwall, 1972). At the surface, clasts have been modified by exposure. Coatings of calcite and silica are common, as well as rock varnish made up of manganese oxides. Additional lithologies that are minor in extent but may have an impact on transport in the alluvium include playa deposits from evaporation in the southeastern part of the Amargosa Desert, calcrete deposits from infiltrating precipitation, and opal and calcite fillings in fractures and spring deposits (National Research Council, 1992). Clay units may also form from the weathering of the alluvium, as evidenced by clay pits in Ash Meadows, and a test hole drilled about 5 km southwest of Lathrop Wells indicates that playa deposits may exist at depths of more than 400 m (Claassen, 1985).

The NRC staff expects that the series of boreholes to be drilled in the alluvium as part of the Nye County Early Warning Drilling Program (EWDP) will provide significant information concerning the geologic and hydrologic characteristics. It is expected that the mineralogy will reflect that used in batch sorption experiments for determining sorption coefficients for radionuclides in tuff. If that is so, the laboratory work needed to address Subissue 1 will also address Subissue 2. Through early 1999, the EWDP had drilled eight wells to the south of YM. Lithologic logs available through the Nye County website (Nye County, 1999) indicate that much of the alluvium consists of valley fill and basin deposits of gravel, silt, and sand varying in thickness from 33 m (110 ft) in well NC-EWDP-3S to more than 490 m (1,618 ft) in well NC-EWDP-2D.

4.2.2.2.2 Aqueous Speciation

Aqueous speciation in the alluvial waters will operate in the same way as speciation in the porous rock, and any differences that might affect alluvial radionuclide transport will be due to differences in aqueous chemistry in the alluvial aquifers relative to waters in the tuffaceous aquifers. Water in the SZ in the Amargosa Valley is typically more saline than SZ waters close to the repository, and is chemically saturated with phases such as montmorillonite and calcite that may have an effect on sorption processes (White, 1979; Claassen, 1985; White and Chuma, 1987). Higher concentrations of carbonate and bicarbonate may also reduce sorption by surface complexation in the alluvium relative to the tuffaceous aquifers.

4.2.2.2.3 Effects of Ligands

Radionuclides will complex with inorganic ligands in the alluvial waters in the same fashion described in Section 4.1.2 for porous rock aqueous speciation. Alluvial aquifer hydrochemistry (White, 1979; Claassen, 1985; White and Chuma, 1987; Perfect, et al., 1995; Oliver and Root, 1997) suggests that carbonate, sulfate, and chloride are present as ligands in greater concentrations in alluvial waters as opposed to tuffaceous aquifers near YM. This may result in the formation of radionuclide complexes that can reduce sorption (Bertetti, et al., 1998; Pabalan, et al., 1998; Turner, et al., 1998a). Heterogeneities in the water chemistry suggest that sorption and other retardation mechanisms will also vary with location in the alluvial aquifers.

Kingston and Whitbeck (1991) report infra-red (IR) spectra analysis of organic molecules in water samples collected from alluvial aquifers in the Amargosa Desert and the NTS. Both fulvic and humic acids were present as coatings on minerals. Kingston and Whitbeck (1991) could not rule out contamination due to pumping oil or fingerprint contamination.

4.2.2.2.4 Radionuclide Concentration

The effect of radionuclide concentration will be the same on alluvial radionuclide transport as it is on porous rock radionuclide transport as discussed in Section 4.1.2. Any differences will depend on the differences in aqueous chemistry and mineralogy between the alluvial groundwaters and the waters from the porous rock. Because the alluvial aquifers are farther from the source, it seems reasonable to expect radionuclide concentrations to be lower than they are close to the repository due to mechanical dispersion and other retardation processes. Source term issues are potentially affected by radionuclide concentrations, but these are considered in detail as part of the ENFE and CLST KTIs.

4.2.2.2.5 Cation Ratio

The cation ratio affects competitive sorption involving radionuclide and nonradioactive species and will be the same for alluvial radionuclide transport as it is for porous rock radionuclide transport as discussed in Section 4.1.2. Any differences will depend on the differences in aqueous chemistry between the alluvial waters and the waters in the tuff aquifers. For example, higher TDS in the alluvial waters may result in competitive sorption for available sorption sites by components such as Ca and Mg.

4.2.2.2.6 Kinetics

The effect of reaction kinetics on alluvial radionuclide transport will be the same as it is on porous rock radionuclide transport, as discussed in Section 4.1.2. Any differences will depend on the differences in aqueous chemistry between the alluvial waters and the waters from the porous rock.

4.2.2.2.7 Temperature/Moisture Dependence

The SZ alluvium in the YM vicinity is not expected to experience significant thermal effects from the repository itself, and radionuclide migration will be controlled by the ambient chemistry and mineralogy of the region. Data from Perfect, et al. (1995) in the vicinity of YM indicate a range in reported sample temperatures in springs and wells from about 2° to 64 °C, with a mean of about 26 °C.

4.3 RADIONUCLIDE TRANSPORT THROUGH FRACTURED ROCK

4.3.1 Review Methods and Acceptance Criteria

DOE considers radionuclide transport a key performance attribute of the natural barrier system in the proposed repository. Retardation of radionuclides in fractures in the UZ and in the SZ constitutes a key element of the NRC subsystem abstraction for PA. DOE must adequately estimate the transport characteristics of the YM site and appropriately consider radionuclide transport through fractures in its assessments of repository performance. The review process should determine which transport processes have been addressed/assumed by DOE. The reviewer should identify first, whether or not the selected retardation processes are appropriate to the YM system, and secondly, whether or not they are addressed adequately for those radionuclides of concern.

The following *Acceptance Criteria* apply to evaluating the DOE estimates and consideration of radionuclide transport through fractures:

1. For estimation of radionuclide transport through fractured rock, DOE has

    a. Determined, through PA calculations, whether radionuclide attenuation processes such as sorption, precipitation, radioactive decay, and colloidal transport are important to performance.

    b. (i) Assumed K_d (or K_A) is zero and that radionuclides travel at the velocity of groundwater flow through fractures, if it has been found that radionuclide attenuation in fractures is unimportant to performance, and it can be demonstrated that this assumption is conservative. In this case Acceptance Criteria 2 and 3 do not have to be met; or, (ii) Demonstrated that Criterion 2 or 3 has been met, if radionuclide attenuation in fractures is important to performance, or if an assumption that K_d (or K_A) is zero in fracture transport is not conservative.

2. For the application of the K_d (K_A) approach, using equation (1) ($R_f = 1 + \rho_b K_d/n$) or equation (13) ($R_f = 1 + AK_A$), DOE has:

    a. Determined the percentage of total groundwater flux that is carried along the flow path through fractures. For that portion flowing through matrix, refer to Acceptance Criteria for Subissue 1. Evaluation of matrix/fracture flux are considered as part of the USFIC KTI (Nuclear Regulatory Commission, 1998b).

    b. Identified flow velocity through fractures. Evaluation of travel time through fractures in the UZ and SZ are considered as part of the USFIC KTI (Nuclear Regulatory Commission, 1998b).

    c. Demonstrated that appropriate values for fracture transport parameters (e.g., K_d (or K_A), A, n, θ, ρ_b), have been adequately considered for each leg of the transport path (UZ , SZ). Detailed evaluation of the hydraulic properties of fractures is being undertaken as part of the USFIC KTI (Nuclear Regulatory Commission, 1998b).

    d. Demonstrated that the three implicit assumptions (i.e., linear isotherm, fast reversible sorption reaction, and constant bulk chemistry) are valid.

3. For the valid application of process models such as surface complexation, ion exchange, precipitation/dissolution, and processes involving colloid material, DOE has:

a. Determined the percentage of total groundwater flux that is carried along the flow path through fractures. For that portion flowing through matrix, refer to Acceptance Criteria for Subissue 1.

b. Identified flow velocity through fractures. Detailed acceptance criteria for fracture flow models are defined in the USFIC KTI (Nuclear Regulatory Commission, 1998b).

c. Demonstrated that appropriate parameter values based, to the extent possible, on laboratory experiments, field tests, and site characterization data, have been used in process models.

d. Demonstrated that the three implicit assumptions (i.e., linear isotherm, fast reversible sorption reaction, and constant bulk chemistry) are valid, if process models are intended to yield a constant retardation parameter [e.g., K_d (or K_A)]; otherwise, determined transport in a dynamic reactive transport system model (e.g., PHREEQC, MULTIFLO, HYDROGEOCHEM, etc.).

4. Where data are not reasonably or practicably obtained, expert judgement has been used and expert elicitation procedures have been adequately documented. If used, expert elicitations were conducted and documented in accordance with the guidance in NUREG-1563 (Nuclear Regulatory Commission, 1996) or other acceptable approaches. It is important to remember that expert elicitation and sensitivity analyses are not to be used as a replacement for experimental and field data, where such data can be reasonably obtained.

5. Data and models have been collected, developed and documented under acceptable QA procedures (e.g., Altman, et al., 1988) or, if data were not collected under an established QA program, they have been qualified under appropriate QA procedures.

4.3.2 Technical Bases for Acceptance Criteria

It is important to note that most, if not all, of the processes and parameters/properties that affect radionuclide transport through fractures are expected to be the same as those identified in Section 4.1.2 for radionuclide transport through porous rock. The magnitude of the process or effect may be different, however, due to differences in the chemical and hydrological system in fractures as compared to matrix. For example, sorption through a surface complexation mechanism will operate in the same fashion in both the fractures and the porous rock, but differences in the water chemistry and mineral chemistry (see Section 4.1.2.) or flow velocity will control the extent to which sorption occurs by this mechanism. The technical bases for the acceptance criteria for radionuclide transport through fractures are generally the same as those described in Section 4.1.2. To avoid duplication, the discussion of the technical bases presented in the next section will be limited to differences that are to be expected given likely variations between the fracture flow system and the matrix flow system. Available information on mineral chemistry of fractured rocks is well documented (Carlos, 1985; 1987; 1989; Carlos, et al., 1991; 1993, 1995a,b; Vaniman, et al., 1996a), but understanding of the continuity of the fracture mineralogy, and the degree to which it inhibits matrix diffusion and provides retardation of radionuclide migration, is limited. Chemistry of the water in fractures is also uncertain, and perhaps best represented through perched water chemistry (Yang, et al., 1996a,b, 1998) and water collected from fracture zones at Rainier Mesa (White, et al., 1980) and in the ESF (Fabryka-Martin, et al., 1996).

The following section expands on the description of process models that affect radionuclide transport through fractured rock and the parameters required for each process. This discussion section is not intended to be exhaustive, and provides only a sample of important processes affecting radionuclide transport.

4.3.2.1 Demonstrating Conservativeness of a No Retardation Assumption

In general, an assumption of zero retardation in a fracture is considered to be conservative. For fracture flow, under steady-state chemical conditions, this would be a valid assumption, and radionuclides would migrate through the fractures at the same velocity as the groundwater. Under other conditions in fracture flow, however, an assumption of zero retardation may not be conservative. The first of these is colloid transport, as discussed in more detail in Section 4.3.2.2.6. Colloid migration may be enhanced relative to fluid flow due to volume exclusion effects and reduced particle/medium interaction. An assumption of zero retardation would not be adequate to consider these effects. The microsphere experiments at the C-Wells complex (Reimus, et al., 1998) indicate that, although filtration of colloids may be significant, transport breakthrough occurs quickly. With the uncertainty in injection time in the microsphere tests, early arrival of colloids at a field scale of 10s of meters may be possible. Also, the colloidal transport of plutonium and other radionuclides from the Benham test (Kersting, et al., 1999) may indicate enhanced radionuclide migration. Also, as discussed previously in Section 4.1.2.2.3.3, assuming some retardation in fractures may be a nonconservative approach. Exercising models with the assumption of zero retardation allows radionuclides to leave the modeled system at a concentration that is generally determined by solubility limits, and decreases away from the source term. Sorption onto fracture-lining minerals under one set of chemical conditions, however, may lead to the creation of a secondary source (Fuentes, et al., 1987; Yeh and Tripathi, 1991). If groundwater chemistry changes under transient conditions, this could lead to a remobilization of radionuclides (reduction in K_d or K_A) for transport. Transient chemical changes in parameters such as ionic strength could also lead to a remobilization of colloid particles that are filtered through chemical attachment (see Section 4.3.2.2.6).

4.3.2.2 Processes Affecting Radionuclide Transport through Fractured Rock

4.3.2.2.1 Surface Complexation

Surface complexation has been identified as a principal means of sorption on oxides and oxyhydroxides of metals such as Fe, Mn, and Si. These are common fracture-lining minerals in the YM system (Carlos, et al., 1993) and may also be created by oxidation of materials introduced during the construction and operation of the repository (e.g., steel containers and rock bolts). Electrostatic surface complexation is a function of surface charge. Titration experiments with oxyhydroxides indicate that surface charge is a complex function of system chemistry, particularly pH (Davis and Kent, 1990; Turner, 1993). For cations such as UO_2^{2+},

NpO_2^+, and Am^{3+}, oxyhydroxides exhibit a sharp sorption edge where, depending on radionuclide concentration and the number of available sites, sorption of cations increases from essentially zero to nearly 100 percent with increasing pH over a relatively narrow pH range; the location of the edge depends on the redox state of the element and the hydrolysis behavior of the element of interest (Dzombak and Morel, 1990; Turner, 1995; Bertetti, et al., 1998; Pabalan, et al., 1998). In the presence of complexing ligands such as CO_3^{2-}, cation sorption typically decreases to zero with further increases in pH beyond the sorption maximum. For anions and oxyanions such as SeO_4^{2-}, the reverse is true; sorption typically decreases in a gradual fashion with increasing pH (Davis and Kent, 1990). Reactive surface areas can be high for minerals such as the amorphous forms of oxyhydroxides, suggesting the potential importance of these minerals as a sorbent phase. In addition, the potential for forming a sorptive oxide coating on less sorptive particles, such as quartz or feldspar, suggests an additional role for these minerals in radionuclide sorption (Robert and Terce, 1989). In transport through fractures, the sorption capacity of the fracture may be limited by sporadic distribution of sorbing phases (Carlos, 1985, 1987, 1989; Carlos, et al., 1991, 1993, 1995a,b; Paces, et al., 1996). In addition, wetting of fracture surfaces may limit the area over which radionuclide-bearing solutions are exposed to sorbing minerals.

Although the SZ waters in the vicinity of YM are undersaturated with respect to calcite, waters in Amargosa Valley and other areas near YM are chemically saturated. Calcite is also present in the tuff aquifers in fractures and lithophysae. For radionuclide sorption, the surface charge of carbonate minerals is dominated by the balance between the dominant cation (Ca^{2+} and/or Mg^{2+}) and the carbonate anion (CO_3^{2-}). For this reason, sorption on carbonates is a complex function of pH, solution chemistry, and PCO_2. Recent efforts have focused on adapting surface complexation models to describe sorption at the carbonate/water interface (van Cappellen, et al., 1993).

As mentioned in Section 4.1.2., recent work with batch experiments suggests that actinide sorption on silicate and aluminosilicate minerals is likely to be controlled by surface complexation processes (Pabalan, et al., 1997; Bertetti, et al., 1998; Turner, et al., 1998a). The sorption "envelope" bounded by sharp decreases in sorption at high and low pH, when expressed in terms of K_d, is sensitive to chemical parameters such as pH and carbonate concentration, but relatively insensitive to mineral type and radionuclide concentration (Bertetti, et al., 1998; Pabalan, et al., 1998). When K_d is normalized to mineral surface area, however, the sorption envelopes of different minerals overlap for a given radionuclide, suggesting that surface area (and by extension, available sorption sites) is a key factor controlling actinide sorption. Modeling results suggest that this dependence is diminished above a threshold value for sorption sites (Turner, 1995). Experiments with different size fractions of crushed tuff indicate that sorption is independent of grain size down to 38 µm (Rogers and Meijer, 1993). The same study also showed that BET surface areas were also relatively insensitive to particle grinding size, suggesting that the experimental conditions were above the threshold site concentration for the radionuclide-water-solid systems studied.

4.3.2.2.2 Ion Exchange

Other sorptive phases, such as clays and zeolites, occur at YM as secondary replacement products. Because of interlayer exchange sites and the large surface area resulting from their layered structure, clays can have a high cation exchange capacity. Smectite, vermiculite, and some kaolinite group clays expand upon interaction with water or organic fluids. This can change the interlayer spacing, and affect the degree to which radionuclides can penetrate the interlayer ion exchange sites and sorb onto clays (Goldberg, et al., 1991). Increasing ionic strengths can reduce interlayer spacing and ion exchange on planar sites. The edge sites (perpendicular to the silicate layers) also exhibit a surface charge that varies as a function of pH in a manner like that for oxides and oxyhydroxides. Actinide sorption on clays is pH-dependent (Zachara and McKinley, 1993; Pabalan and Turner, 1997; Turner, et al., 1998a).

Zeolites such as clinoptilolite, heulandite, and analcime, are also likely to be important for retarding radionuclide transport at YM. Zeolites exhibit a fixed charge developed by substitution of Al^{3+} for Si^{4+} in the zeolite structure that is compensated by Na^+, K^+, Ca^{2+}, and Mg^{2+} in the intracrystalline exchange sites. Sorption is typically by way of ion exchange in the intracrystalline sites (Davis and Kent, 1990; Murphy and Pabalan, 1994), particularly for the alkaline and alkaline earth elements such as the short-lived radioisotopes of Cs^+ and Sr^{2+}, but there also appears to be a component of pH-dependent surface charge as well (Pabalan, et al., 1993; Pabalan and Turner, 1993).

Actinide sorption on clays and zeolites demonstrates behavior typical of surface complexation, but at low pH and low ionic strength, sorption is likely to occur by an ion exchange mechanism (Turner, et al., 1996; Pabalan and Turner, 1997; Turner, et al., 1998a). At higher pH, actinide speciation, particularly hydrolysis, tends to result in complexes that are too large to fit in the exchange structures. Higher ionic strengths on the order of 0.1 M tend to suppress ion exchange through filling of available sites by common ions such as Na^+ and Ca^{2+}.

Radionuclides sorbed on fracture surfaces by reversible surface complexation or ion exchange mechanisms are available for remobilization if water chemistry in the fracture should change (Yeh and Tripathi, 1991). This can include changes in pH, ionic strength, and concentration of major cations and ligands such as Ca^{2+}, Na^{2+}, and CO_3^{2-}.

4.3.2.2.3 Precipitation/Dissolution

One mechanism for removing radionuclides from solution is the precipitation of stoichiometric radioelement compounds or coprecipitation as impurities in other minerals. Changes in system chemistry parameters such as Eh, pH, temperature, and component concentration, influence the solubility of radionuclide-bearing minerals. For example, reduction of UO_2^{2+} to U^{4+} greatly reduces uranium in solution through precipitation of reduced uranium minerals such as uraninite (e.g., Langmuir, 1987) that have lower solubility limits. Under oxidizing conditions, increases in dissolved silica and other species can stabilize minerals such as soddyite and uranophane. These and other minerals will sequester not only U, but also other radionuclides such as Np and Pu through coprecipitation (Murphy and Prikryl, 1996; Buck, et al., 1998). Uncertainties in thermodynamic and kinetic properties, and variable mineral stoichiometry, make realistic modeling of precipitation and dissolution of these mineral phases difficult.

4.3.2.2.4 Radioactive Decay

The technical basis for consideration of radioactive decay is provided in Section 4.1.2.

4.3.2.2.5 Matrix Diffusion and Imbibition

In addition to movement of a radionuclide-bearing fluid in response to system gradients in temperature, pressure, and chemistry, solute can also move in and out of the fluid parcel. These migration processes include: (1) thermal or Soret diffusion in response to the temperature gradient; (2) ultrafiltration or reverse osmosis in response to pressure gradients; and (3) mass diffusion in response to concentration gradients.

Chemical osmosis (the movement of water in response to concentration gradients) has also been suggested by Carnahan (1984) as a major factor in fluid flux. Numerical simulations indicate that water flux in hydrologically saturated clays from less to more concentrated zones can be as much as three to four orders of magnitude greater than the Darcy flux. This is counterbalanced by the flux of solute back across the membrane by pressure gradients (ultrafiltration/reverse osmosis). In coupled systems, Carnahan (1984) indicates that reverse osmosis is of minor significance compared to chemical osmosis.

Matrix diffusion transport models are based on a conceptual model of the existence of two regions in a porous medium (Winterle, 1998). In one region, water is mobile and free to transport ions in solution by advective and dispersive processes through a system of connected fractures and macropores. In the second region, water is considered immobile (or stagnant) in dead-end pore spaces. Mass transfer between the two regions is by diffusion alone in response to concentration gradients.

Experimental evidence suggests radionuclide diffusion into the tuff matrix at YM (Walter, 1985; Triay, et al., 1997). For example, experiments with diffusion cells and rock beakers indicate that diffusion occurs at a slower rate in devitrified tuff relative to zeolitized tuff (Triay, et al., 1997). In addition, radionuclide diffusion (TcO^{-}_{4}) is, in all cases, slower than tritiated water (HTO); calculated effective diffusion coefficients (D_{eff}) ranged from 1×10^{-10} to 3.5×10^{-10} m^2/s for HTO and 1×10^{-11} to 4.9×10^{-11} m^2/s for TcO^{-}_{4}. For sorbing radionuclides such as NpO_2^+, PuO_2^+, and UO_2^{2+} diffusion is a function of both tuff type and water chemistry (Triay, et al., 1997). In the experiments, diffusion of sorbing radionuclides was consistent with a two-stage conceptual model, with rapid diffusion into larger pores and microfractures, and slower diffusion into narrower pores. Matrix diffusion transport modeling is being examined in detail as part of the USFIC KTI (Nuclear Regulatory Commission, 1998b). Findings from this effort should be used in evaluating the acceptability of DOE submittals.

A retardation mechanism that is potentially important at YM is migration of water in response to suction pressure gradients from fractures, where transport may be relatively rapid, into the matrix where flow is slow. Once imbibed into the matrix, not only is flow slower, increased exposure to larger surface areas of sorbing minerals may enhance retardation by sorption and ion exchange. Diffusion into the matrix should also serve to reduce differences in aqueous concentrations between the fracture and the matrix. Water samples collected from the UZ and from perched water bodies in the YM vicinity differ in chloride concentration. For example, in well UZ-16 at a depth of 528 m, there is an order of magnitude greater chloride concentration in pore waters relative to perched water (Triay, et al., 1997; Yang, et al., 1996a,b). This suggests that matrix diffusion in response to chloride gradients between the pores and perched water in fractures is slow relative to the infiltration rate. Field studies at the Nopal I uranium deposit in the Peña Blanca mining district, Chihuahua, Mexico (Pearcy, et al., 1995) suggest that diffusion into relatively homogeneous matrix (i.e., free of fractures and other heterogeneities) is of limited importance in uranium transport. Instead, uranium transport in fractured tuff appears to be dominated by fracture flow and precipitation of a suite of secondary uranyl minerals that proceeds with time through hydrated uranyl oxides to uranyl silicates and adsorption and/or coprecipitation onto Fe oxyhydroxides and clays. Similar paragenesis has been observed in long-term drip experiments using synthetic groundwaters related to that from the J-13 well at YM and unirradiated UO_2 (Wronkiewicz, et al., 1992). Additional research in matrix diffusion at YM and approaches to modeling matrix diffusion may be developed as part of the USFIC KTI (Nuclear Regulatory Commission, 1998b).

4.3.2.2.6 Colloid Transport

4.3.2.2.6.1 Colloid Stability

If actinides and other radioelements can sorb onto pseudocolloids or form true colloids, the stability of the particles in suspension is of critical importance in colloid mediated transport. True colloid stabilization is favored under alkaline conditions, especially in the case of highly charged, redox-sensitive species such as actinides (Maiti, et al., 1989; Choppin and Mathur, 1991). In the case of pseudocolloids, particles may be introduced through the nucleation and growth of crystalline and amorphous mineral phases in response to chemical supersaturation. In a groundwater system, particles may also be released from the aquifer matrix to solution. This release may be due to electrostatic dispersion brought about by changes in solution ionic strength, mechanical disruption of primary and secondary minerals owing to shearing and grinding of mineral surfaces by hydrodynamic forces or autogrinding between suspended particles, or dissolution of a more soluble matrix to expose and release the colloid. Human activity associated with a HLW repository may also introduce colloidal materials in the form of organics associated with waste treatment, dissolution of vitrified waste-forms, and organic matter used in drilling, construction, and repository operations (Travis and Nuttall, 1985b). Corrosion products from the EBS may also serve as sources for pseudocolloid formation.

For metal oxyhydroxides, particle stability is a function of pH, Eh, particle size, and the total concentration of the metal (e.g., Fe, Mn, Al, Ti, Si) in solution. The presence of other ligands such as HCO_3^- and SO_4^{2-} and CO_3^{2-} can also affect the formation of oxides by consuming metal ions in the precipitation of carbonate and sulfate solids. If changes in solution chemistry result in desorption of radioelements, they are free to sorb onto the immobile medium.

4.3.2.2.6.2 Colloid Filtration

McDowell-Boyer, et al. (1986) divided filtration processes into three basic classes: surface (cake) filtration, straining, and physical-chemical filtration. Surface filtration involves building a barrier at the water/pore interface. This type of filtration occurs when the particles are too large to enter the pores of the medium. As the particles are stopped at the surface, they are held in place by the fluid flow, and a mat or cake is gradually formed. With time, the filter cake thickens, and its porosity and permeability decrease through compression. Fluid flow through the mat decreases, and there is a pressure drop across the cake. Filter cake permeability is also a function of particle aggregation. Destabilized colloidal suspensions (e.g., high ionic strength) tend to form a more porous arrangement than those cakes formed from highly dispersed stable suspensions (McDowell-Boyer, et al., 1986). If the particles are small enough to enter the porous medium, the tortuous path they must follow may eventually lead to a constriction that is too small for them to pass through. This leads to a straining of the colloids from solution.

Colloid transport at YM is likely to be complicated by the unsaturated conditions, partial coverage of pores and fracture walls, and the presence of two-phase (air-water) flow. Most of the research on colloid formation and transport, however, is based on studies of saturated media, and colloid transport through unsaturated media such as YM is poorly understood. The presence of a gas phase may influence particle transport by particle attachment to the bubble surface (Wan and Wilson, 1994). For example, a recent study of the effect of hydrologically unsaturated conditions on colloid transport indicated that hydrophilic colloids are preferentially sorbed at the gas/water interface while hydrophobic colloids sorb at both the gas/water and solid/water interfaces (Wan and Wilson, 1994).

Natural Colloid Material

Well J-13 in Jackass Flats to the east of YM was sampled for natural colloids (Kerrisk, 1987; Department of Energy, 1988). Filtering of 9,300 L of water through the membrane filters yielded about 2.7×10^{-5} g/L of particulate material. The bulk of the material was retained by the 400-nm filter assemblies, and the 5–400 nm filtrate accounted for less than 1 percent of the total yield. Analysis of the 400-nm to 10-μm fraction with SEM and emission spectroscopy indicated a composition dominated by Si-Fe-Ca, with minor Al, while the 5–400 nm fraction was predominantly Na-Si with minor amounts of Ca and Fe. Equilibrium speciation calculations performed with the MINTEQA2 code (Allison, et al., 1991) for the J-13 well water in contact with atmosphere, indicate that, although J-13 water is undersaturated with respect to calcite, groundwater is supersaturated with respect to ferrihydrite, kaolinite, montmorillonite, and several other minerals that may form coatings or natural colloids favorable to the formation of pseudocolloids. Organic material is also reported in J-13 well water (Means, et al., 1983; Department of Energy, 1988). Total organic carbon is reported at 0.14±0.05 mg/L, and compounds greater than 1,000 g/mol make up more than 50 percent of the material. Based on these analyses, there seems to be at least some natural colloidal matter suitable for the formation of pseudocolloids.

In addition to natural colloids already present in the YM environment, the construction, operation, and permanent closure of the repository may introduce additional material that may act as sources for colloids. These sources can include corrosion of the canisters and glass wasteforms, degradation of backfill materials such as clays (Travis and Nuttall, 1985b; Salbu, et al., 1987), drilling muds, and the introduction of organic materials such as EDTA during the processing of the waste (Means, et al., 1978a,b; Means and Wijayaratne, 1982) and construction of the repository.

True Colloid Formation

Several of the radionuclides predicted to be important in repository performance (Kerrisk, 1985) are known to form true radiocolloids through hydrolysis, polymerization, and crystallization

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(Patera, et al., 1990). Both Am and Pu exhibited appreciable colloidal formation at high pH, possibly as $Am(OH)_3$ and $Pu(OH)_4$, respectively (Olofsson, et al., 1982a,b; 1985). In contrast, Np colloid formation was negligible, except at pH > 10 for high ionic strength solutions (1 M $NaClO_4$). Kim, et al. (1987) also proposed the generation of centrifugable Am true radiocolloids in experiments performed with natural groundwaters containing significant amounts of dissolved organic carbon (DOC). Hobart, et al. (1989) reported on the preparation and analysis of Pu(IV) colloidal sols, and observed that the redox potentials of the colloids differed significantly from those predicted for dissolved Pu^{+4} ions. Using autocorrelation photon spectroscopy, Rundberg, et al. (1988) determined that the diameter and density of ^{242}Pu colloids were 2.9±0.2 nm and 9.0 g/cm^3, respectively. Rundberg, et al. (1988) also observed that a ^{239}Pu colloid formed in the experiment remained stable at a particle size of 180 nm for over 2 yr.

4.3.2.2.6.3 Colloid Transport in the Yucca Mountain Vicinity

Recent field studies involving groundwater pumped from wells downgradient from an underground detonation cavity suggest colloidal transport of radionuclides (Kersting and Thompson, 1997; Smith, 1997; Thompson, 1998; Kersting, et al., 1999). Ultrafiltration indicates that isotopes of Co, Cs, Eu and Pu were detected on colloidal material consisting of mordenite, illite, and cristobalite. The isotopic signature of $^{240}Pu/^{239}Pu$ suggests that plutonium associated with a colloid phase migrated about 1.3 km downgradient from the Benham test cavity at Pahute Mesa on the NTS. Tracer tests at the C-Well complex (UE-25 c#1, c#2, and c#3) indicate that colloid-sized particles (0.36 µm diameter polystyrene microspheres) migrated 31.7 m through the Lower Bullfrog tuff, but were attenuated by filtration, with only about 11 percent recovery after 2,650 hr (Reimus and Turin, 1997).

Travis and Nuttall (1985b) proposed a conceptual model of colloid transport at the YM site and simulated the results using the TRACR3D numerical code (Travis and Nuttall, 1987). From mercury porosimetry, most of the matrix porosity in the Topopah Spring Tuff, the host rock at the proposed horizon for the underground repository, is believed to be less than 1 µm, and 50 percent of the pores are smaller than 0.1 µm. Since the larger pores are the last to saturate, it is also likely that matrix flow will be confined to the smaller pores under unsaturated conditions. Therefore, in the case of matrix flow, colloidal transport of radionuclides would be limited to particles of approximately 100 nm or less. Fracture transport is possible, and fracture apertures of 50 to 250 µm in the Topopah Spring Tuff (Travis and Nuttall, 1985b) would allow for transport of larger particles. However, Travis and Nuttall (1985b) argued that the low pore water velocities (2 mm/yr for matrix flow, 2 m/yr for fracture flow) anticipated for the YM environment are on the order of molecular diffusion rates, allowing radionuclides to diffuse out of the particles into a dissolved ionic form that is more readily sorbed onto the tuff matrix.

4.3.2.2 Parameters/Properties Affecting Radionuclide Transport through Fractured Rock

4.3.2.2.1 Fracture Mineralogy

Fracture mineralogy studies at YM have focused on the Paintbrush Group, the Calico Hills Formation, and the Crater Flat Group, and are based on a suite of seven drill holes (Vaniman, et al., 1996a). Calcite, smectite, silica minerals, zeolites, and iron and manganese oxyhydroxides line fractures in the tuffs at YM (Carlos, 1985, 1987, 1989; Carlos, et al., 1991, 1993, 1995a,b; Paces, et al., 1996). The most common minerals are silica polymorphs (quartz, tridymite, cristobalite, and opal), zeolites (clinoptilolite, analcime, heulandite, mordenite, stellerite), calcite, and manganese oxyhydroxide (cryptomelane, hollandite, rancieite, lithiophorite). In the Paintbrush Group above the static water level (SWL), fracture mineralogy is variable, and does not necessarily correlate with the surrounding matrix mineralogy. In some cases, zeolites occur in fractures even though the tuff is devitrified and nonzeolitic (Vaniman, et al., 1996a). Smectite is typically widespread as a fracture-lining mineral.

In the Calico Hills Formation and the Crater Flat Group, zeolite occurrences are generally limited to zeolitized matrix, and the type of fracture-lining zeolite corresponds to the matrix zeolite (e.g., clinoptilolite in fractures is limited to clinoptilolite-containing strata). Tridymite occurs in early fractures related to lithophysal cavities and is increasingly replaced by cristobalite or quartz with depth. Manganese oxides with nonlithophysal quartz and mordenite are common coatings on planar cooling fractures. Zeolites, mordenite, heulandite/clinoptilolite, and stellerite are dominant in later fractures. Smectite and calcite occur commonly in fractures as late-forming minerals in variable amounts (Carlos, et al., 1991). Although, mordenite and euhedral heulandite are common fracture minerals in the Topopah Spring Tuff above the water table, mordenite is rare and heulandite is absent from fractures in this member below the water table in samples taken from borehole J-13 (Carlos, 1989).

In the SZ, fractures crossing zeolitic horizons tend to be dominated by zeolites similar to the surrounding matrix (Vaniman, et al., 1996a). Fractures that cross devitrified horizons are more complex, dominated by iron and manganese oxyhydroxides, with subordinant amounts of zeolite, smectite, and calcite. Some oxide banding in the matrix suggests diffusion from the fracture into the matrix (Vaniman, et al., 1996a).

The zeolites in the Paintbrush Group tend to be calcic in composition, while zeolites in the Calico Hills and Crater Flat units tend to be sodic. Dating of fracture mineralogy is uncertain, but fracture-lining zeolites seem to have been formed at the time of the alteration of the tuff. For example, there is a general increase to the north in analcime at the expense of clinoptilolite/mordenite that may result from hydrothermal activity related to the Timber Mountain caldera (Bish and Aronson, 1993; Vaniman, et al., 1996a). Low-temperature fracture coating minerals tend to be limited to fractures with apertures greater than a few millimeters, and the degree and type of mineralization can vary with aperture along a single fracture (Paces, et al., 1996). Mineralization can also change with fracture orientation and dip (Paces, et al., 1996).

Geochemical evidence suggests that groundwater flow through the tuff aquifers in the vicinity of YM is channelized (Murphy, 1995; Wittmeyer, et al., 1995). The occurrence of vein-filling carbonate in regions where groundwater is undersaturated with respect to calcite indicates that portions of the rock are effectively isolated from current groundwater flow. In addition, stable isotope data (e.g., Whelan and Stuckless, 1992) indicate that calcites more than 300 m below the water table are compatible with Paleozoic carbonates ($\delta^{13}C = -5.2$ to -2.3‰) rather than the water currently in the tuff aquifer ($\delta^{13}C = -11.4$ to -4.9‰). Channeling is also likely in the Paleozoic carbonate aquifer. Radioisotope data (^{14}C) and stable isotope data for springs in Ash Meadows indicate that flow and recharge occur relatively quickly. The preservation of recharge isotopic signatures in spring waters suggests that flow paths may be quite different for different springs, and that mixing and dispersion are limited (Winograd and Pearson, 1976). Recent work analyzing the ^{14}C composition of fracture coatings (Simmons, 1996; Paces, et al., 1996) report ages of about 16,000 to 44,000 yr. In contrast, ages calculated using $^{230}Th/U$ measurements range from about 28,000 to more than 500,000 yr. Fine layering in the coating minerals suggest episodic precipitation/dissolution, however, and may add uncertainty to the isotopic measurement by mixing older and younger minerals in the analyses.

Fracture-lining minerals identified at YM include zeolites, Fe- and Mn-oxyhydroxides, and clays, all of which are known to be strong sorbers of radioelements. For example, in the Peña Blanca natural analog site in Chihuahua, Mexico, uranium is strongly associated with fracture-filling Fe-oxyhydroxides (Leslie, et al., 1993; Pearcy, et al., 1995). Autoradiography studies of PuO_2^+ sorption by fracture lining minerals indicate that altered orthopyroxenes and oxide minerals show high retention for plutonium; smectite shows a wider-spread, but weaker association (Vaniman, et al., 1996b).

Fracture-lining minerals may also plug fractures, reducing fracture permeability. Murphy (1995) used carbonate chemistry to suggest that fractures containing calcite are isolated from the current SZ groundwater system. Alteration surrounding the Papoose Lake sill, intruded into tuff near the eastern edge of the NTS, also suggests that silica migration from tuff heated and altered by the basaltic sill has precipitated quartz, plugging fractures and reducing porosity and permeability (Matyskiela, 1997). Mineral precipitation may also armor fractures, reducing interaction between the tuff and the matrix. For example, near the Papoose Lake sill, precipitation of cristobalite and clinoptilolite within pores less than 1 cm from fracture walls suggests mobilization and diffusion of silica into the matrix, where it precipitated and reduced matrix porosity (Matyskiela, 1997). Silica transport modeling studies support a monotonically decreasing silica gradient from the fracture wall into the tuff, with complete plugging of porosity at distances of about 10 mm. Although the temperatures adjacent to the sill were higher than those anticipated for the far field at YM, it does demonstrate the possible effects of mineral precipitation on hydrologic flow and transport. Field evidence at the Peña Blanca site also suggests that uranium diffusion from fractures into the matrix is limited to the scale of millimeters or less in relatively unfractured tuff (Pearcy, et al., 1995; Pickett and Murphy, 1997; Prikryl, et al., 1997).

Fracture coatings of readily dissolved radionuclide-bearing minerals may, however, provide a means of enhancing radionuclide migration through the UZ. For example, Bradbury, et al. (1988) propose that flow from the matrix to the fractures, accompanied by evaporation, can serve to concentrate radionuclides at the fracture surface. During episodic fracture flow, these radionuclides would be more accessible and readily dissolved again for transport through the fracture flow system.

4.3.2.2.2 Fracture Geometry and Orientation

Fracture geometry is an important control on fracture transport of radionuclides. Fracture geometry includes fracture aperture, trace length, roughness, interconnectedness, orientation, and density. Fracture geometry is defined by the scale at which observations are made, which may range from kilometers to nanometers. In practice, fracture geometries are usually defined in operational terms based on the techniques employed. Techniques range from analysis of satellite imagery (100s to 10s of km), to various field mapping approaches (km to cm), to microscopic observations (mm to nm). The scale at which fracture geometry is considered for radionuclide transport should be chosen to be relevant to the problem at hand. It is essential to bear in mind the operational definition employed. For example, measurements of fracture density necessarily have some operational threshold of observation; fractures below that threshold should be demonstrably unimportant to the process being evaluated using the given fracture density.

Fractures at YM have been characterized for over 17 yr in support of many aspects of site characterization (Sweetkind and Williams-Stroud, 1996). Initial studies were associated with surface-based mapping; most recently, detailed fracture characterization is being carried out in the ESF and in the Enhanced Characterization of the Repository Block (ECRB) cross drift. Additional fracture data are available from boreholes at the site. Because characterization is limited to exposures such as outcrops, cleared pavements, boreholes, the ESF, and the ECRB cross drift, available data do not represent all lithologic units equally well, and it is difficult to generalize observations or to treat the data statistically for the entire YM system. For example, slip and dilation tendency analysis and long-term pump tests of aquifers in the YM region suggest that there is anisotropy in aquifer transmissivity to the east of the repository that is due to fracture orientation and *in situ* stress (Ferrill, et al., 1999). Generalization is further hampered by differences in methodology and dimensionality (1D line surveys, 2D pavement maps, and full periphery ESF fracture maps) (Barton, et al., 1993).

For PA calculations of fracture transport, it is necessary to translate from mechanical descriptions of fracture geometries to effective hydraulic properties (e.g., hydraulic conductivity) and parameters that allow calculation of chemical interactions (e.g., effective surface areas). Methods for making such translations are not well-established. For example, surface area is an essential parameter for sorption calculations. The effective sorptive surface area depends on bulk system generalizations of the gross area of fractures along which radionuclide transport fluids are envisioned to flow, as well as fracture roughness and the available surface areas of sorptive minerals on the fracture walls. Fracture characterization and fracture density are being investigated as part of the Structural Deformation and Seismicity KTI.

4.3.2.2.3 Aqueous Speciation

Aqueous speciation in the fracture will operate in the same way as speciation in the matrix zones, and any differences that might affect radionuclide transport through the fractures will be due in part to differences in aqueous chemistry in the fracture relative to waters in the porous rock. For samples from Rainier Mesa (White, et al., 1980), the pH for fracture waters is slightly lower than interstitial waters, suggesting that actinide sorption by surface complexation will vary between fractures and pores, but the difference in pH is small. Porewaters from the vadose zone at Rainier Mesa also tend to have lower equilibrium CO_2 pressures for a given pH relative to waters in the fractures, suggesting that the effect of carbonate on sorption will be slightly less at a given pH in the matrix. Porewater chemistry suggests that Ca-Cl-SO_4-CO_3 chemistry will tend to control speciation as compared to the likely sodium bicarbonate waters in the fractures (based on perched water chemistry). In addition, the expected higher TDS in the porewaters may have an effect on speciation. However, besides perched water chemistry and the fracture water data at Rainier Mesa, there is little detailed information available on fracture water chemistry in the YM vicinity with which to constrain likely differences in aqueous speciation between fractures and the matrix.

4.3.2.2.4 Effects of Ligands

The presence of ligands such as HCO_3^- and SO_4^{2-} can also influence radionuclide migration by the precipitation of carbonate and sulfate solids to sequester radioelements, either as end-member solids or through coprecipitation. Solubility limits are controlled to some extent by system pH. Because of the potential effects of carbonate aqueous chemistry and the ready extent to which carbon dioxide dissolves into solution, radionuclide complexing and precipitation will also be controlled to some degree by the PCO_2 (Langmuir, 1997). For example, for $pH > 5.5$, UO_2^{2+} exhibits a higher solubility with increasing PCO_2. In general, PCO_2 in typical groundwaters (and the YM groundwaters) is above atmospheric ($10^{-3.5}$ bars) (Murphy and Pabalan, 1994).

4.3.2.2.5 Radionuclide Concentration

Formation of polynuclear species is suppressed at lower concentrations, leading to a dominance of mononuclear species. Also, if radionuclide concentrations are high enough, saturation may be reached with respect to a mineral phase, depending on the concentration of other components and fluid chemical parameters, such as pH.

4.3.2.2.6 Cation Ratio

Competitive sorption includes competition among different radionuclides for available sorption sites, as well as competition by common major dissolved constituents in solution such as Ca^{2+}, Mg^{2+}, and CO_3^{2-}. Competitive sorption experiments by Hsi (1981) suggest that Ca^{2+} and Mg^{2+} in concentrations of 10^{-3} M have relatively little effect on uranium ($\sum UO_2^{2+} = 10^{-5}$ M) sorption on Fe-oxyhydroxides. Surface complexation modeling studies (Bradbury and Baeyens, 1992; 1993), however, predicted that 10^{-6} M Ca^{2+} reduced Np ($\sum NpO_2^{+} = 2 \times 10^{-11}$ M) sorption on ferrihydrite by more than an order of magnitude at $pH > 8$. Increasing Ca^{2+} concentration increased the effect over a larger range in pH ($pH > 7$). In addition, recent experimental evidence suggests that aqueous carbonate species may compete for sorption sites (van Geen, et al., 1994). Surveys relating colloid particle concentration to cation concentration found that increased concentrations of Ca^{2+} and Mg^{2+} were more effective at destabilizing colloid suspensions than increases in monovalent cations such as Na^+ (Degueldre, 1993; Degueldre, et al., 1996).

4.3.2.2.7 Rate Constant

In characterizations of the YM site geochemical systems, relations among some species can be described by chemical equilibrium relations. Chemical equilibrium offers a powerful predictive capability, as well as constraints on kinetic descriptions of irreversible processes. Nevertheless, some critical thermodynamic data are dubious, including data for the properties of secondary mineral solid solutions and aqueous species at elevated temperatures. Furthermore, metastable conditions are common, particularly in low-temperature systems (Essene and Peacor, 1995), and for some oxidation-reduction reactions (Lindberg and

Runnells, 1984). In general, differences in rates among individual reactions lead to states approximating partial equilibrium in geochemical systems. Reactions that are not at equilibrium progress at rates that depend strongly on temperature and the degree of disequilibrium, and the rates of heterogeneous reactions depend on the properties of phase boundaries, such as mineral-solution interfaces.

Mass transfer calculations that account for partial equilibrium and reaction kinetics in gas-water-rock interactions have provided geochemical models related to the YM site (Kerrisk, 1983; Ogard and Kerrisk, 1984; Delany, 1985; Arthur and Murphy, 1989; Murphy, 1993; Murphy and Pabalan, 1994). Aqueous silica concentration and CO_2 pressure have been shown to be particularly important in defining the solid-phase assemblage and the aqueous-solution composition (Murphy and Pabalan, 1994; Murphy, et al., 1996). At present, these models are limited principally by the lack of thermodynamic and kinetic data. However, there have been several recent attempts to obtain such data by experimental and estimation techniques (e.g., Bowers and Burns, 1990; Johnson, et al., 1991; Ransom and Helgeson, 1994; Murphy, et al., 1996) that, in some cases, appear to yield inconsistent results. Calculations of time-dependent processes are further hampered by the difficulty in realistically characterizing spatial heterogeneity and reactive surfaces in geologic environments.

4.3.2.2.8 Temperature/Moisture Dependence

Most sorption experiments are run at room temperature (20 to 30 °C), and the effects of elevated temperature are poorly understood. Machesky, et al. (1994) indicates that the zero-point-of-charge (pH_{ZPC}) of rutile decreases with increasing temperature. This change suggests that negative charge development is enhanced for oxyhydroxides with increasing temperature and that the pH edge for cation sorption would move to lower pH values at higher temperatures. In addition, increased temperature may age mineral surfaces and reduce the reversibility of sorption by incorporating radionuclides in the crystal structure (e.g., Ford, et al., 1997). Limited batch data for temperatures up to 85 °C suggest that sorption coefficients (K_d) either remain constant or increase with increasing temperature for Am, Ba, Ce, Cs, Eu, Pu, Sr, and U on crushed tuff materials (Meijer, 1990). This is also the assumption made in current DOE TSPA transport models (TRW Environmental Safety Systems, Inc., 1995). However, there is a lack of sample characterization before and after sorption, and large experimental uncertainties persist.

4.4 NUCLEAR CRITICALITY IN THE FAR FIELD

4.4.1 Review Methods and Acceptance Criteria

This subissue is limited to consideration of criticality resulting from radionuclide transport and reconcentration in the far field. Criticality issues related to canister and waste form design issues will be considered as part of the CLST KTI and the ENFE KTI.

The review process should determine whether nuclear criticality due to radionuclide transport has been considered by DOE. The reviewer should identify first, if the criticality scenarios considered are appropriate to the YM system, and second, whether they are addressed adequately for those radionuclides of concern.

As specified in 10 CFR 60.131(h), nuclear criticality issues are considered in the context of the requirement that "...all systems for processing, transporting, handling, storage, retrieval, emplacement, and isolation of radioactive waste shall be designed to ensure that criticality is not possible...." The presence of fissile radionuclides such as ^{235}U and ^{239}Pu in HLW creates a potential for sustained neutron chain reaction (criticality event). Among scenarios for repository criticality is the possibility that fissile radionuclides will be transported from a breached WP and re-deposited in a critical configuration in the far field. Potential effects on repository performance of criticality in the far field include an increase in the fission product inventory, a decrease in the fissile radionuclide inventory, and a change in the hydrologic characteristics of the transport pathway due to a local thermal pulse.

The acceptance criteria developed for far-field nuclear criticality are limited to consideration of criticality resulting from radionuclide transport out of the repository drift. Criticality issues related to canister and waste form design issues will be considered as part of the CLST KTI and issues related to criticality within the near field but external to the WP are considered under the ENFE KTI. Some overlap is implied in this distinction, because transport out of the drift may still be subject to near-field effects. For this reason, consideration is given here only to transport unaffected by near-field conditions.

The review process should determine whether nuclear criticality due to radionuclide transport has been considered adequately by DOE. The reviewer should identify first, if the criticality scenarios considered are appropriate to the YM system, and second, whether they are addressed adequately for those radionuclides of concern.

The following *Acceptance Criteria* apply to evaluating the nuclear criticality as a result of radionuclide transport:

1. In all analyses related to criticality due to radionuclide transport to the far field, the DOE has:

    a. Properly considered site characteristics. Analyses are consistent with hydrology, geology, and geochemistry observed during site characterization in the YM system. These data should include realistic rock chemistry, rock porosity, and water chemistry.

    b. Properly considered repository, WP, and waste form design in establishing initial and boundary conditions. Parameters and conceptual models for nuclear criticality as a result of radionuclide transport to the far field are consistent with the current repository and waste form design for the YM repository.

    c. Where process modeling studies have been used, documented preferred and alternative conceptual models that are supported by available data, analyses, and interpretations, and are both internally consistent and consistent with other applications of radionuclide transport models. Adequate basis is provided for excluding potentially adverse phenomena.

   d. Demonstrated that mathematical models are consistent with conceptual models based on field data and field observations at the site. Mathematical model limitations and uncertainties in modeling nuclear criticality due to radionuclide transport are defined and documented. Models are validated by comparison with data from field, laboratory, and natural analog studies.

   e. Performed sensitivity and uncertainty analyses (including consideration of alternative conceptual models) to determine if models are overly optimistic and to help determine whether additional new data are needed to better define ranges of input parameters.

   f. Collected, developed, and documented data and models under acceptable QA procedures (e.g., Altman et al., 1988). Where necessary, data qualification plans are acceptable, and data uncertainties have been identified and documented. Data uncertainties are propagated correctly or are conservative with regard to repository performance. It should be verified that there are no deficiency reports, concerning data quality in relation to nuclear criticality as a result of radionuclide transport, that have not been closed.

   g. Where data are not reasonably or practicably obtained, used expert judgement appropriately and adequately documented expert elicitation procedures. If used, expert elicitations were conducted and documented in accordance with the guidance in NUREG-1563 (Nuclear Regulatory Commission, 1996) or other acceptable approaches.

2. The DOE has established if criticality in the far field has consequences that affect repository performance. In this analysis, the DOE has:

   a. Used appropriate models for estimating worst-case radionuclide inventory increases due to far field criticality events.

   b. Evaluated the effects of criticality event thermal output in the far field, with consideration of coupled thermal-hydrologic-chemical processes that may affect hydrologic conditions.

   c. Appropriately applied criticality effects in TSPA models assessing performance consequences. The DOE has used model parameter estimates that ensure that the analysis is not overly optimistic. Such parameters include radionuclide inventory increase and conservative estimates of the number and timing of far field criticality events. Performance consequences are evaluated in the context of uncertainties and sensitivities established for TSPA.

3. If the DOE has demonstrated that criticality due to radionuclide transport to the far field has negligible impact on repository performance, then no further acceptance criteria apply. If the DOE has not demonstrated that criticality due to radionuclide transport to the far field has negligible impact on repository performance, then the DOE shall demonstrate that scenarios for forming critical configurations in the far field due to

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radionuclide transport are not credible. In establishing scenarios for far field criticality, DOE has:

a. Demonstrated that important mass transfer and mass transport processes and mechanisms affecting formation of both a critical mass and configuration are plausible for the YM environment.

b. Demonstrated that the method for establishing scenarios has a reasonable assurance of not excluding any credible scenarios. Preferred and alternative conceptual models have been documented and are supported by available data, analyses, and interpretations. and are internally consistent.

c. Provided conceptual models and quantitative values for effective neutron multiplication factors (k_{eff}) to demonstrate whether a given configuration of fissile radionuclides will remain subcritical ($k_{eff} < 1$) or become critical ($k_{eff} \geq 1$).

d. Provided reasonable assurance that exclusion of configurations based on an estimated $k_{eff} < 1$ has effectively demonstrated that those configurations are not credible. For example, the DOE may establish a safety factor by establishing a lower value of k_{eff} as a cutoff for configurations considered not credible.

e. Established an appropriate probability screening level for estimating the credibility of criticality for a given configuration.

The technical bases for the acceptance criteria for nuclear criticality as a result of radionuclide transport are given in the next section. These bases are primarily focused on explaining what aspects of transport may be important to nuclear criticality at YM given the current understanding of the YM system. The sophistication of the analysis of nuclear criticality as a result of radionuclide transport that could be conducted and found acceptable by the NRC staff is dependent on the available information, any plans to obtain additional information as part of the long term testing program, and the ability of PA codes to model nuclear criticality as a result of radionuclide transport.

4.4.2 Technical Bases for Acceptance Criteria

As noted by Choi and Pigford (1997), thermally fissile materials (TFM) scheduled for long-term geologic disposal in the proposed HLW repository at YM can theoretically reach criticality in a geologic medium. These may include weapons-grade Pu, highly enriched uranium (HEU) from naval and research reactors, small amounts of plutonium and enriched uranium from commercial and DOE-owned spent nuclear fuel (SNF), and other heavy elements such as neptunium. At present, the design options for disposal of weapons-grade plutonium and HEU have not been finalized, and it is uncertain if and how these materials will be placed in the proposed repository.

4.4.2.1 Principles of Criticality Safety

A detailed discussion of chemical parameters affecting criticality safety in the Hanford Tank Waste Remediation system is provided in Pabalan et al. (1997), and only a brief summary is provided here. Before a self-sustained neutron chain reaction, or critical state, can be achieved, a number of physical conditions must exist. One required condition is the presence of a sufficient amount of fissile material to absorb neutrons and undergo fission. Each fission event generates several high-energy neutrons. These neutrons undergo interactions in which they either lose energy, are absorbed, or are lost from the system by leakage. The critical state of a system is determined by the number of neutrons lost by absorption or leakage relative to the number of neutrons from fission events that are available to produce subsequent fissions. If more neutrons are absorbed or lost by leakage than are produced by fission, then the system is considered to be subcritical. If an equal number of neutrons are produced as are lost or absorbed, then the system is considered to be critical. If more neutrons are produced than are lost or absorbed, then the system is considered to be supercritical.

The critical state is mathematically represented by a parameter called k_{eff}, which is defined as the number of neutrons in one generation divided by the number of neutrons in the preceding generation. A critical state has a neutron population that remains constant, and the value of k_{eff} is equal to one. A subcritical system has a neutron population that decreases in time, and the value of k_{eff} is less than one. A supercritical system has a neutron population that increases in time, and the value of k_{eff} is greater than one. If the size of the system is effectively infinite and has no neutron leakage, the parameter of interest is called k_∞. The value of k_{eff} is always less than or equal to the value of k_∞. Typically, an upper bound for subcritical conditions is to have a calculated k_{eff} value of less than 0.95, with a 95-percent confidence level.

For TFMs, fission occurs more readily after neutrons have undergone several scattering reactions and their energy has decreased such that the neutrons are in thermal equilibrium with the scattering medium. The process of reducing the neutron energy, known as "slowing down" or "moderation," is most effectively accomplished by materials of low atomic mass and high ratios of neutron scattering to absorption coefficients, such as hydrogen. These materials are called moderators. At optimum moderation, a minimum amount of fissile material is required to sustain a chain reaction. At other than optimum moderation, more fissile material is required to reach criticality. The amount of fissile material required for criticality is also affected by the concentration of the fissile material, the geometry of the system containing the fissile material, and the presence (or absence) of other materials that compete with the fissile material for absorption of neutrons.

4.4.2.2 Parameters That Affect Criticality

To prevent inadvertent criticality in a system, specific controls and limitations are placed on the factors that affect criticality. For HLW disposal operations, the factors most important to criticality include: (i) concentration of TFM, principally ^{239}Pu, (ii) the amount and property of neutron absorbers or moderators present with the fissile material, (iii) the geometry of the system containing the fissile material, and (iv) the presence or absence of neutron reflectors adjacent to the system. Each of these parameters is discussed in more detail in the following sections.

4.4.2.2.1 Fissile Material Concentration

To achieve criticality, the TFM must be present in a certain concentrations, regardless of the size of the system. This concentration is based on assumptions regarding solids, water, and mixture characteristics present in the proposed repository environment. In pure water, for example, a ^{239}Pu concentration of 7.2 g/L is generally reported as the minimum critical concentration of plutonium (Knief, 1992).

Table 4-2. The minimum subcritical ratio for various waste components (from Braun, et al., 1994)

Component	Minimum Subcritical Ratio (mass of X/mass of ^{239}Pu)
Al	910
Cr	135
Ni	105
N	61
Nitrate	270
Na	360
Si	1400
Mn	32
Fe	160
U (natural)	770

4.4.2.2.2 Neutron Absorbers

Neutron absorbers reduce the reactivity of any fissile mixture by reducing the thermal neutron flux in the mixture. These materials generally absorb neutrons and release gamma or alpha particles, which do not contribute to further fission events. There is a unique minimum absorber-to-plutonium mass ratio for all absorbers, above which the system will remain subcritical, independent of any other influences. One of the most effective absorber materials, boron, is likely to be engineered into wasteforms for disposal. Exclusion of neutron absorbers such as boron leads to a conservative estimate of the subcritical margin of safety.

Braun, et al. (1994) presented results of criticality analyses that were conducted to determine the subcritical nature of tank wastes at Hanford, Washington. The analyses were based on calculating the minimum absorber-to-plutonium (X/Pu) mass ratio necessary to ensure subcriticality of the wastes assuming optimum moderation. Table 4-2 presents minimum subcritical mass ratios for various waste components taken from Braun, et al. (1994). The minimum subcritical ratios determine the minimum relative concentrations of the absorber materials which, if present individually with the Pu, would assure subcriticality for any degree of moderation.[1] In the case of Hanford wastes, which are multicomponent systems containing two or more neutron absorbers, subcritically is guaranteed if the sum of the fractions of the minimum X/Pu subcritical ratios for the various neutron absorbers present in the waste is greater than 1 (e.g., a system with a mass ratio of Mn to Pu of 16 and a mass ratio of Fe to Pu of 81 would be subcritical).[2]

If a mechanism for concentrating Pu exists that can lead to Pu concentrations above the 7.2 g/L required for a k_∞ of 1 for a pure water- ^{239}Pu system (Knief, 1992), the required absorber concentration to guarantee subcriticality becomes quite large. For example, for a mixture composed solely of iron, ^{239}Pu, and water for a situation that has concentrated ^{239}Pu to a level of 10.0 g/L, an iron concentration of 1,600 g/L is necessary to ensure subcriticality. This required amount of iron would increase for larger Pu concentrations.

4.4.2.2.3 Geometry

Geometry plays a role in determining subcritical limits because of its impact on neutron leakage. Neutrons that leak out of the system will not contribute to any further fissions; therefore, reducing the number of neutrons that escape the system will increase the reactivity of the system. If the geometries for HLW disposal can be shown to be subcritical for infinite conditions, any geometry of finite size in the absence of reflectors will be even more subcritical.

The effects of geometry are typically discussed in terms of a sphere. This is because a sphere is the most reactive geometry and thus constitutes the bounding case. Other typical, easily modeled geometries include infinite slabs and infinite-length cylinders.

4.4.2.2.4 Neutron Reflectors

Neutron reflectors surrounding the TFM may increase the reactivity of the system by returning neutrons that have leaked out of the system to the fissile material where they are able to contribute to further fissions. The reflectors will only reduce the losses from geometry effects so, for conservative calculations that assume infinite dimensions, reflectors will have no effect. Although it is unknown whether reflectors will be present around the fissile material, calculations

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[1] Waste systems are composed of many components, and it is more correct to take into account the presence of all neutron absorbers to demonstrate the margin of subcriticality. This procedure can be accomplished by defining a parameter, referred to as the *fraction of the actual-to-minimum subcritical ratios*, that assigns a value to the relative worth of each component as a neutron absorber. This parameter is defined as the actual X/Pu mass ratio for a neutron absorber divided by the corresponding minimum subcritical mass ratio (e.g., table 5-1). The resulting fraction is a measure of the quantity of absorber present relative to that required to ensure subcriticality. The larger the fraction of the actual-to-minimum subcritical ratio, the more subcritical is the waste composition. When the fraction of the actual-to-minimum subcritical ratios exceeds unity, subcriticality is ensured regardless of the degree of moderation and reflection (Braun et al., 1994).

[2] Mathematically, the sum of the fractions is given by the formula

$$\sum_{j=1}^{N} \frac{(X_j/\mathrm{Pu})_{\mathrm{actual}}}{(X_j/\mathrm{Pu})_{\mathrm{subcritical}}} \geq 1$$

that take credit for neutron leakage losses must take into account the effects of neutron reflectors if they are present.

4.4.2.3 Theoretical Autocatalytic Criticality for High-Level Radioactive Waste

While the waste canisters and wasteforms are intact, design features to prevent criticality are expected to function as planned, and criticality should not be an issue (Bowman and Venneri, 1995; Choi and Pigford, 1997). Following canister failure, however, Bowman and Venneri (1995) presented a conceptual model where added neutron absorbers (e.g., boron and lithium) and subcritical concentrations of ^{239}Pu, ^{235}U and other TFM are mobilized from wasteforms in the YM repository environment, and the TFM deposited in a concentration and geometry sufficient to reach criticality. Bowman and Venneri (1995) also proposed a series of feedback mechanisms, with the rock itself acting as a moderator in a low-water environment; as the system reaches criticality, water would boil off and disperse Pu into a greater volume of rubbilized rock, eventually creating a geometry that is autocatalytic (or self-enhancing).

In general, Bowman and Venneri (1995) considered a spherical geometry of homogeneous mixtures of ^{239}Pu with water and SiO_2 as a proxy for rock. For the idealized spherical Pu-H_2O-SiO_2 geometry considered, Bowman and Venneri (1995) noted that a sphere of about 25 cm radius is the smallest geometry that can sustain an autocatalytic reaction and, depending on the mole fraction of silica, Bowman and Venneri (1995) proposed that a spherical mass of as little as 2 kg of ^{239}Pu may be enough for autocatalytic criticality. Canavan et al. (1995) provide some qualitative discussion of the validity and probability of the Bowman and Venneri (1995) hypothesis. A similar approach for ^{235}U would require an even larger critical mass than ^{239}Pu. Bowman and Venneri (1995) use the natural reactors at Oklo, Gabon (Smellie, 1995) as evidence that such reactions have occurred in nature.

A number of internal reviews of the hypothesis presented by Bowman and Venneri (1995) were conducted at Los Alamos National Laboratory, and several critiques of the hypothesis proposed by Bowman and Venneri (1995) have been prepared (Murphy et al., 1995; Parks et al., 1995; Van Konynenburg, 1995). Most of these critiques focus on several key aspects of the Bowman-Venneri hypothesis that limit its applicability in the YM environment, including:

- The lack of specificity on plausible radionuclide transport mechanisms that could lead to assembling a spherical geometry. One proposed mechanism is colloid transport into fractures surrounding the wasteform. It still is not clear whether colloid transport through the UZ can move and concentrate the amounts of plutonium that are necessary. At present, experiments suggest that glass does not alter to form pure plutonium phases, but instead alters to a suite of clays and secondary minerals (Bates et al., 1992). In addition, if plutonium is bound to existing particles and transported as pseudocolloids, the mass of plutonium required for criticality will be larger than that required for a pure plutonium phase.

- Low plutonium solubility limits (10^{-6} to 10^{-12} molar) that potentially require large volumes of water to provide the mass of ^{239}Pu necessary for autocatalytic criticality. For the lower solubility, it is estimated that tens of cubic kilometers of water would have to transport through a 100 cm radius sphere to transport the potentially critical 15 kg of ^{239}Pu by means of dissolution and re-deposition (Murphy et al., 1995).

- The poor analogy between SiO_2 and the host rock at YM. Other constituents in the waste (e.g., ^{238}U), rock (e.g., K, Al, and Na) and in the groundwater (Cl) would serve as neutron absorbers, requiring significantly larger amounts of TFM for criticality, changing the dynamic behavior of the critical system, and possibly eliminating the possibility of self-enhancing autocriticality. Also, dissolution of poisons such as boron and lithium is dependent on system chemistry, and preferential leaching scenarios relative to silica are likely to be much more complex than the simple model proposed by Bowman and Venneri (1995).

- Consideration of realistic porosity and hydrologic saturation would greatly limit the mole fraction of water in the system, eliminating all but the largest geometries (and greatest masses of ^{239}Pu) from consideration in the YM system. Also, the heterogeneity of the YM system makes it difficult to develop the idealized spherical geometry and homogeneous mixture considered by Bowman and Venneri (1995) (Van Konynenburg, 1995).

- The time scales involved in geologic radionuclide transport are much longer than the relatively short assembly times required to promote autocatalytic behavior, making disassembly of the critical geometry likely. If criticality were obtained, energy release would be more likely to be at low power (Van Konynenburg,1995), and as in the natural reactors at Oklo, water would be driven out and the reactors would shut down. In addition, with yield strength of the rock less than the infinitely rigid medium assumed in the blast dynamic calculations of Bowman and Venneri (1995), it is possible that rock would deform in response to the temperatures and pressures generated by the proposed nuclear excursion, changing the neutronics of the system and stopping the supercritical event.

In summary, these arguments suggest that this particular mechanism for far-field criticality has a minimal likelihood of occurrence.

5.0 STATUS OF ISSUE RESOLUTION AT THE STAFF LEVEL

5.1 STATUS OF SUBISSUE 1—RADIONUCLIDE TRANSPORT THROUGH POROUS ROCK

5.1.1 Criterion-By-Criterion Analysis

Table 5-1 lists radioelements that have been considered in previous PA of the proposed YM HLW Repository and radioelements that have been used in sorption experiments but are not expected to affect performance (e.g., chemical analogues for those radionuclides that could affect performance but are difficult to handle in laboratory experiments). Shaded rows indicate those radioelements with isotopes (^{14}C, ^{99}Tc, ^{129}I, ^{79}Se, ^{231}Pa, ^{234}U, ^{237}Np, ^{239}Pu, and ^{242}Pu) considered in DOE TPSA-VA (U.S. Department of Energy, 1998c). Against each of the radioelements, the table lists acceptance criteria. Check marks indicate the acceptance criterion has been fulfilled, or at least partially fulfilled. For example, a check mark in column 2b2 indicates batch sorption experiments were performed using site-specific materials. It is not intended to indicate that all sets of solid/groundwater conditions expected for the YM system have been tested. Furthermore, one should not expect that all boxes will have to be checked for issue resolution. Some boxes are mutually exclusive. For example, by assuming K_d is zero, as in the case for C, I, and Cl, the need for satisfying Criteria 2 and 3 is eliminated.

The key to this table is as follows:

1a	Radioelement has been included in PA
1b	K_d is assumed to be zero
2a	Demonstrated isotropic homogeneous porous media flow
2b1	K_d determined experimentally in batch sorption tests
2b2	Used site specific materials in batch sorption tests
2b3	Performed crushed tuff flow-through column experiment
2b4	Performed intact rock flow-through column experiment
2b5	Performed diffusion experiment
2b6	Performed unsaturated flow experiment
2b7	Used process model to determine constant K_d
2c1	Demonstrated linear isotherm by determining K_d as a function of radionuclide concentration
2c2	Demonstrated fast ion exchange or adsorption reaction
2c3	Demonstrated constant bulk chemistry
3a	Demonstrated isotropic homogeneous porous media flow
3b	Demonstrated use of appropriate parameters for process models
3c	Demonstrated three implicit assumptions are correct
4	Expert elicitation
5	Quality assurance

Table 5-1. Status of subissue 1 radionuclide transport through porous rock. Some boxes are mutually exclusive, and not all boxes will have to be checked for issue resolution.

	Criterion 1		Criterion 2											Criterion 3			Crit. 4	Crit. 5
	1a	1b	2a	2b							2c			3a	3b	3c		
				2b1	2b2	2b3	2b4	2b5	2b6	2b7	2c1	2c2	2c3					
Am	✓			✓	✓			✓		✓					✓		✓	
Pu	✓			✓	✓	✓		✓		✓	✓	✓			✓		✓	✓
U	✓			✓	✓			✓		✓					✓		✓	✓
Th	✓			✓	✓												✓	
Ra	✓			✓	✓												✓	
Pb	✓			✓													✓	
Np	✓			✓	✓	✓		✓		✓		✓			✓		✓	✓
Pa	✓			✓	✓												✓	
Sn	✓			✓	✓												✓	
Ni	✓			✓	✓												✓	
Cs	✓			✓	✓			✓		✓	✓				✓		✓	
Sr	✓			✓	✓			✓			✓						✓	
C	✓	✓								✓					✓		✓	
Ac				✓														
Sm				✓														
Nb	✓			✓	✓													
Zr				✓														
I	✓	✓								✓					✓		✓	
Tc	✓	✓		✓	✓	✓		✓				✓					✓	
Cl	✓	✓															✓	
Se	✓			✓	✓		✓		✓	✓					✓		✓	
Ce				✓	✓						✓							
Cm																		
Eu				✓	✓						✓							

5.1.1.1 CRITERION 1a. Determined, Through Sensitivity Analysis, Whether Radionuclide Attenuation Processes Such as Sorption, Precipitation, Radioactive Decay, and Colloidal Filtration Are Important to Performance

The radionuclides for which the boxes are checked have been evaluated in previous PAs (see Section 3.2). This criterion is included to allow DOE to determine the importance of a given radionuclide without having to perform laboratory experiments. For example, radionuclides with short half-lives and small inventories may contribute so little to the dose that

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they need not be considered. The use of sensitivity analysis to eliminate from further consideration the retardation of certain radionuclides requires greater reliance on other aspects of the repository performance. This approach, however, cannot be used to the extreme, whereby all the reliance is placed on one aspect of repository performance to the exclusion of all others. The satisfactory demonstration of multiple barriers is treated as a subissue of TSPAI IRSR.

The staff considers that this acceptance criterion has been met for radionuclides important to performance. However, as processes, conditions, and conceptual models are revised based on new site characterization information and repository designs, it is expected that new sensitivity analyses would be needed. The only situation where this criterion would not be met would occur if DOE failed to consider a radionuclide in its PA that the NRC staff considered to be important. If sensitivity analyses have been performed for radionuclides important to performance, the staff considers this criterion met.

5.1.1.2 CRITERION 1b. Assumed K_d Is Zero and Radionuclides Travel at the Rate of Groundwater Flow, If it Has Been Found That Radionuclide Attenuation Is Unimportant to Performance and it Can Be Demonstrated That this Assumption Is Conservative; No Other Acceptance Criteria for this Subissue Need Be Met, Or, Demonstrate That Criterion 2 or 3 Has Been Met, If Radionuclide Attenuation in Porous Rock Is Important to Performance or If an Assumption That K_d Is Zero in Porous Rock Is Not Conservative.

This criterion has been used for carbon. Carbon, technetium, iodine, and chlorine occur predominately as anions and, as such, experience limited attraction to the negatively charged surfaces of the minerals along the flowpath. The staff agrees with the selection of C, Tc, I, and Cl as having a K_d of zero, for use in PAs. The staff recognizes, however, that there may be other elements or species that, under certain situations, have a K_d of zero.

There are examples where multiple species of a single radionuclide exist in solution at the same time. Some species can be cations and others, anions. The retardation of the species varies as a function of their charge and size. A classic example, occurred at the Cambric site where ruthenium, with a nonzero K_d, was observed at a sampling well before it was expected. It was later discovered that ruthenium is present in both cationic and anionic forms, and the negatively-charged ruthenate ion contributed to the early breakthrough.

Plutonium is another radionuclide with multiple species, including cationic as well as anionic and colloidal forms. Triay, et al. (1997) and Thompson (1989) show that some plutonium travels unretarded in crushed tuff column experiments. The plutonium and ruthenium examples demonstrate the importance of performing flow-through column tests for identifying mobile species (see status of Criterion 2b3 below).

5.1.1.3 CRITERION 2a. Demonstrated That the Portion of the Flow Path to Which Equation (1) Applies Acts as an Isotropic Homogeneous Porous Medium

This criterion is generally independent of the radionuclide migrating through the medium. However, radionuclide size and charge can exclude certain radionuclide species from the isotropic homogeneous medium in favor of the heterogeneous features. The C-Well tests provide an example that suggests a portion of the flow path is not acting as an isotropic homogeneous porous medium.

Currently, the only portions of the flowpath considered to be an isotropic homogeneous porous medium in the NRC's TPA are the nonwelded vitric unit of the Calico Hills and the alluvium (See Subissue 2, Radionuclide Transport through Alluvium). The reason the vitric unit is considered a porous medium is because its matrix permeability is considered high enough to accommodate the percolation rates expected for YM. On the other hand, the nonwelded zeolite unit of the Calico Hills has a matrix permeability that may accommodate a relatively small portion of the percolation rate. Consequently, most of the water bypasses the zeolite unit in fractures.

5.1.1.4 CRITERION 2b. Determined Appropriate Values for Parameters, K_d, n or θ, and ρ_b

5.1.1.4.1 CRITERION 2b1. Sorption Coefficient Has Been Determined Using a Batch Sorption Test

Any radionuclide for which an experimentally determined K_d has been determined using a batch sorption test has this box checked in the table above. This includes radionuclides whose batch sorption tests have not involved site-specific materials, along with radionuclides whose batch sorption tests have. The radionuclides for which nonsite-specific batch sorption tests have been performed are lead, actinium, samarium, and zirconium. The NRC staff considers the sorption coefficients determined from nonsite-specific batch sorption experiments much less certain than those determined using site-specific materials.

5.1.1.4.2 CRITERION 2b2. Sorption Coefficient Has Been Determined From Sorption Test Using Site-Specific Materials

Batch sorption experiments using site-specific materials have been performed yielding K_d values for americium, plutonium, uranium, thorium, radium, neptunium, protactinium, tin, nickel, cesium, strontium, niobium, technetium, selenium, cerium, and europium. Triay, et al. (1997) states that batch sorption experiments involving protactinium and site-specific materials have only been performed at pH values 6.3 to 6.7. Consequently, the report recommends that sorption experiments involving protactinium be performed at pH values between 7 and 9 to match the expected pH of waters at YM. The NRC staff agrees with this recommendation.

Plutonium batch sorption experiments have been performed using site-specific materials. These materials included rocks such as zeolitic tuff, vitric tuff, devitrified tuff, minerals such as clinoptilolite, albite, quartz, synthetic hematite, montmorillonite, calcite, gibbsite, and groundwaters including J-13 and UE-25p#1.

Sorption experiments involving selenium have only used J-13 water. Triay, et al. (1997) states that changes in divalent ion concentration may affect selenium sorption more than changes in pH. The NRC staff agrees with the recommendation in that report that additional experiments using groundwaters with higher divalent ion concentrations (e.g., UE-25p#1) should be performed.

Sorption of uranium in J-13 well water onto YM tuffs has been described by Triay, et al. (1997). The concentrations of uranium in the initial solutions range from 33 ppm down to 0.049 ppm. The silica concentration is 57 ppm, and the final pH ranges from 6.9 to 8.6, depending upon whether the experiments were performed in a glovebox maintaining elevated CO_2 pressure or at atmospheric pressure. Equilibrium calculations using PHREEQC with the WATEQ4F.DAT database and the log K for the dissolution reaction of soddyite from the EQ3/EQ6 database, suggest that the initial solutions for the sorption experiments may have been supersaturated with respect to soddyite. Triay, et al. (1997) explain the importance of ensuring that a sorption experiment involves sorption and not precipitation. If precipitation has occurred, the resulting partition coefficient is not a K_d to be used in equation (1).

It is possible that the precipitation of soddyite is inhibited. Sorption of uranium onto the solid could be occurring without the precipitation reaction also occurring. However, if precipitation reactions are kinetically inhibited, the use of solubility limits calculated using thermodynamic data to constrain radionuclide concentrations would be brought into question. The Generic Technical Position on Radionuclide Solubilities (Brooks, et al., 1984) recommends constraints on radionuclide concentrations be based on solubility experiments that approach equilibrium from both undersaturation and oversaturation.

Sorption of uranium as a function of radionuclide concentration was determined resulting in sorption isotherms. Since the dissolution of soddyite depends on pH, uranyl, and silica concentration in solution, the nonvertical isotherm for uranium does not necessarily preclude the possibility of precipitation of soddyite. Variations in uranyl concentration could be compensated for by variations in pH and silica concentration, and the solution could still be in equilibrium with soddyite.

Another possible explanation for the suggestion of supersaturation with respect to soddyite is that the thermodynamic parameters used for calculating the dissolution of soddyite are incorrect. The database of EQ3/EQ6 uses the estimated free energy of formation of soddyite from Hemingway (1982). Two more recent studies have yielded much higher free energies of formation of soddyite. Nguyen, et al. (1992) and Moll, et al. (1996) experimentally determined synthetic soddyite solubility. These solubility experiments approached equilibrium from undersaturation. The final equilibrated solutions were analyzed for their uranyl and silica concentrations and the Gibbs free energy of formation was calculated. However, the measured silica concentrations (300 ppm) in the final equilibrated solutions exceed solubility of amorphous silica. Consequently, the results of these studies can be challenged.

Triay, et al. (1997) note that unsaturated zone water that is relatively high in calcium and magnesium, may have low K_d values for uranium, due to competing ions for sorption sites. The NRC staff agrees with the recommendation in the Triay, et al. (1997) report that experiments using high calcium and magnesium, low carbonate, unsaturated zone water composition with pH ranging from 6 to 9, and batch sorption experiments involving high total carbonate and high calcium and magnesium (e.g., UE-25p#1) should be performed.

Thorium sorption experiments involving site-specific materials were reported by Rundberg, et al. (1985) and Thomas (1988). Triay, et al. (1997) suggests that fine colloidal particles in solution may have contributed to uncertainty in the K_d values for thorium. Such a suggestion would indicate confirmatory tests are needed.

Wolfsberg (1978) describes sorption-desorption studies of NTS alluvium that included experiments with niobium. The NRC staff considers these experiments involved material that may approximate material expected to be encountered in the alluvial portion of the flowpath from the repository. Sorption of niobium on other site-specific material using appropriate groundwaters has not been performed. Triay, et al. (1997) suggests that fine colloidal particles in solution may contribute to uncertainty in the K_d values for niobium. Such a suggestion would indicate that confirmatory tests are needed.

Tin sorption experiments have been performed using site-specific rock samples and J-13 and UE-25p#1 groundwaters. Consequently, Criteria 2b1 and 2b2 have been met for tin. However, as with thorium, Triay, et al. (1997) states the large range in sorption coefficients may reflect the presence of colloidal-size particles in the solution phase. Such a suggestion would indicate that confirmatory tests are needed.

Triay, et al. (1997) groups actinium, americium, and samarium together, along with cerium and europium, due to the similarities in their chemical speciation in aqueous solution and their sorption reactions. All exist in the +3 oxidation state and form carbonate, phosphate, and hydroxide complexes. Sorption coefficients for cerium, europium, and americium were determined for a variety of Yucca Mountain rock samples and J-13 and UE-25p#1 groundwaters. Triay, et al. (1997) states that "the main uncertainty regarding the surficial behavior of americium appears to be the degree to which it is mobilized through colloidal transport (for example, Penrose, et al., 1990)." Such a suggestion would indicate confirmatory tests are needed.

Triay, et al. (1997) groups cesium, radium, and strontium together because they exist as simple ions. Their sorption reactions largely involve ion exchange. The batch sorption tests for these radionuclides were performed using site-specific solids and groundwaters including J-13 and UE-25p#1. The NRC staff considers this criterion has been met for these radionuclides.

Nickel sorption has been determined on YM materials including devitrified, zeolitic and vitric tuff from several groundwaters in the pH range from 8.3 to 9.0. The limited range in pH for the nickel experiments is the reason the NRC staff considers this criterion only partially met for nickel. However, it may be possible to calculate the sorption coefficient at lower pH values.

Sorption of lead, samarium, zirconium, and actinium have not been determined using site-specific materials. Consequently, the criterion has not been met for these elements.

Neptunium sorption has been determined using site-specific materials. They include devitrified, vitric and zeolitic tuff, clinoptilolite, hematite, calcite, albite and quartz, J-13 and UE-25p#1 well waters at pH values of 7, 8.5 and 9.0. This criterion has been met for neptunium.

5.1.1.4.3 CRITERION 2b3. Performed Crushed Tuff Flow-through Column Experiment

Column experiments have been performed to confirm batch sorption K_d values for plutonium, neptunium, and technetium. The criterion has not been met for any other elements listed in the table 5-1. The DOE Site Characterization Plan (SCP) (U.S. Department of Energy, 1988) originally called for these tests to be performed with plutonium, americium, neptunium, uranium, technetium, cesium, strontium and barium.

For those radionuclides that may be mobilized as colloids (e.g., americium, plutonium, thorium, neptunium, tin, actinium, samarium, niobium, cerium, and europium), meeting this criterion has added importance, since the K_d from the batch test may have provided an inaccurate measure of the mobility of the radionuclide. Batch experiments need to be designed and conducted, however, to analyze for the presence of colloids. Additionally, for radionuclides that exist as multiple species in solution, the crushed tuff column experiment can be used to determine if the different species can migrate at different rates in an advective system.

Triay, et al. (1996a) demonstrated that the K_d from batch sorption experiments could be used to predict breakthrough for neptunium through crushed zeolitic, devitrified, and vitric tuffaceous material. The apparent dispersivity of the neptunium elution curves through the zeolitic and vitric tuffs led Triay, et al. (1996a) to suggest that "sorption is either nonlinear, irreversible, or noninstantaneous, which means the transport cannot be completely described using a sorption distribution coefficient." However, the report continues that "the use of a batch sorption distribution coefficient to calculate neptunium transport through YM tuffs would result in conservative values for neptunium release." Consequently, the NRC staff considers that this criterion has been met for neptunium.

Triay, et al. (1997) describes crushed tuff column experiments illustrating plutonium migration. Figures 98 through 109 from that summary and synthesis report illustrate elution curves for plutonium and tritium through devitrified, zeolitic, and vitric crushed tuff with J-13 and UE-25p#1 well waters. This document lacks some details needed for the correct interpretation of the elution curves. The report states that "we inject an aliquot of the radionuclide solution (tritiated water or $^{239}PuO_2^+$ in the appropriate groundwater) and then used a syringe pump to elute the radionuclide through the column." This statement is interpreted to mean that radionuclide is not added continuously, but instead, as a pulse, which is then flushed through the column with uncontaminated groundwater. The ordinate is labeled "Cumulative Concentration (C/C_o)" and the abscissa is labeled "Cumulative Volume (mL)." From the shape of the curves and the assumption that the radionuclide is added as a pulse, it is assumed that the y-axis should be labeled "Cumulative Relative Mass." That way the curves approach unity with increased volume, as they do.

The elution curve for plutonium through devitrified tuff with J-13 well water (Figure 98) shows that approximately 85% of the plutonium added to the column moves through the system unretarded. Of the remaining plutonium, 5% elutes and 10% stays on the column until the experiment is terminated (20 hrs and 55 mL through column). (The elution curve for tritium reaches a maximum 1.2 in Figure 100 in Triay, et al., (1997). The explanation for C/C_0 for tritium exceeding 1 is unknown.)

The elution curve for plutonium through zeolitic tuff is similar to that through devitrified tuff. Figure 106 of Triay, et al. (1997) illustrates that 50% of the plutonium is eluted shortly after the unretarded tritium peak with UE-25p#1 well water. With J-13 water, only 20% of the added plutonium is eluted in the course of the experiment. When vitric tuff is present the elution curves are very shallow indicating gradual release. The amounts eluted range from 8% to 30% for the experiment's duration. Figures 108 and 109 (Triay, et al., 1997)indicate that flow rates affect the shape of the elution curve, with slower flow rates resulting in significantly reduced percentage of plutonium eluting.

Considering the thermodynamic calculations using EQ3 do not agree with observed speciation, the recognition that multiple species do exist, including colloidal forms, and K_d values from batch sorption tests ranging from 20 mL/g (for devitrified tuff) to 2,000 mL/g (for vitric tuff) are inconsistent with crushed tuff column experiments where significant portions of plutonium are eluted unretarded, the NRC staff concludes this criterion has not been met for plutonium. Triay, et al. (1997) state on page 144 that "The shape of the elution curves for plutonium indicates that use of K_d values to predict plutonium transport through YM tuffs will predict plutonium releases conservatively." On the same page, Figure 98 shows 85% of the plutonium eluting unretarded. It is not clear to the NRC staff how it can be proposed that batch sorption tests provide information for conservatively estimating plutonium transport.

5.1.1.4.4 CRITERION 2b4. Performed Intact Rock Flow-through Column Experiment

Conca and Triay (1996) describes a study of selenium migration through unsaturated intact rock. It was demonstrated that the migration of selenium could be estimated conservatively from batch sorption tests. The advantage of this type of experiment over that of batch sorption test is that the sorbing surfaces are likely to be in a more natural state. This criterion is met for selenium. Similar experiments have not been performed using any of the other radionuclides.

5.1.1.4.5 CRITERION 2b5. Performed Diffusion Experiment

Diffusion experiments have been performed for tritium, technetium, neptunium, americium, strontium, cesium, and barium. The advantage of this experimental approach is that the sorbing surfaces are likely to be undisturbed. Consequently, there should be little concern normally associated with crushing, such as generating greater surface areas, and creating fresh surfaces that may be unnaturally sorptive. Figure 132 of Triay, et al. (1997) illustrates a comparison between calculated cesium concentration in a system in which diffusion and sorption are occurring and the actual observed concentrations. The calculated concentrations assumed reversible, instantaneous, linear sorption. The discrepancy between the observed and calculated concentrations suggests that one or more of the assumptions are incorrect. Since isotherms have been measured for cesium (See Criterion 2c1), it may be possible to adjust this comparison.

5.1.1.4.6 CRITERION 2b6. Performed Unsaturated Flow Experiment

Conca and Triay (1996) describe solid-rock column unsaturated flow experiments performed using the unsaturated flow apparatus (UFA). The criterion is met for selenium. The Busted Butte Unsaturated Transport tests are expected to provide additional important information on unsaturated flow and transport in the Topopah Spring and Calico Hills tuffs at the field scale (Bussod and Turin, 1999). Tracers injected during Phase 1 and Phase 2 have included fluorescine and bromide as conservative elements, lithium, and five separate polyfluorinated benzoic acids. Polystyrene latex microspheres are being injected to investigate colloid movement, and a number of reactive tracers such as nickel, molybdenum, cerium, and rhenium are being injected as analogs for radionuclide transport (Bussod and Turin, 1999; U.S. Department of Energy, 1998c, Volume 1, Appendix C). Phase 3 experiments are still under development, and may include the use of radionuclide tracers (Bussod and Turin, 1999).

5.1.1.4.7 CRITERION 2b7. Used Process Model to Determine Constant K_d

Experimental evidence indicates that sorption behavior is dependent on the physicochemical conditions in the system of interest. Geochemical sorption models to describe these dependencies, and the necessary model parameters, have been summarized and described in several reports (e.g., Davis and Kent, 1990; Serne, et al., 1990; Turner, 1993; Paviet-Hartmann and Triay, 1997). These include ion exchange and surface complexation approaches to sorption, both of which have been used to describe radionuclide sorption mechanisms and characterize the geochemical dependence of radionuclide sorption (e.g., Turner, 1995; Triay, et al., 1997; Paviet-Hartmann and Triay, 1997). Process models have been applied to some extent to sorption of several radioelements of interest in PA, including: neptunium, plutonium, uranium, americium, carbon, cesium, iodine, and selenium (Bradbury and Baeyens, 1993; Dzombak and Morel, 1990; Turner, 1995; Triay, et al., 1997; Paviet-Hartmann and Triay, 1997). The model parameters are calibrated against a set of well-constrained experiments. Process models typically use thermodynamic data for the radioelement of interest to calculate aqueous speciation and determine the amount of radioelement dissolved in solution and the amount sorbed onto the solid. This output can then be used to calculate K_d as a function of chemistry.

Calibrated process models can be used to calculate K_d values under conditions beyond the limited set of conditions for which batch or column experimental sorption data are available (Turner, 1998; Turner, et al., 1998b, 1999). Even in extrapolating model results, however, the application of the K_d approach is subject to the same conditions as the use of batch sorption results. As discussed previously, the assumption of a constant K_d in PA implies that the physicochemical system does not change significantly over the time period of interest. It also requires that the physicochemical conditions remain constant at the level of discretization of the PA model abstraction.

5.1.1.5 CRITERION 2c. Demonstrated That the Three Implicit Assumptions (i.e., Linear Isotherm, Fast Reversible Sorption Reaction, and Constant Bulk Chemistry) Are Valid

5.1.1.5.1 CRITERION 2c1. Demonstrated Linear Isotherm by Determining K_d as a Function of Radionuclide Concentration

Sorption isotherms have been determined for plutonium, uranium, neptunium, cesium, strontium, cerium, and europium. In comparison, the SCP (U.S. Department of Energy, 1988) had listed only four radioelements for which isotherms would be determined. These radioelements were plutonium, uranium, neptunium, and americium. The sorption isotherm for europium, a homologue for americium, but with a lower specific activity, and, thus, less of a problem experimentally, has been determined instead of the isotherm for americium.

Triay, et al., (1997) state that the sorption isotherms for plutonium "are generally nonlinear." The nonlinearity in the isotherms is expressed as a curve with the convex side up. As discussed in Section 4, isotherms with convex side up produce self-sharpening fronts and can be used to predict breakthrough. Consequently, this criterion is met for plutonium.

The isotherms for neptunium are generally linear. Only near the solubility limit for neptunium is there some nonlinearity. Uranium isotherms are nonlinear but convex up and so can be used to estimate retardation. Isotherms for cesium, strontium, cerium, and europium are best fitted to a nonlinear Freundlich isotherm, with convex side up.

5.1.1.5.2 CRITERION 2c2. Demonstrated Fast Ion Exchange or Adsorption Reaction

Triay, et al. (1996a) investigated the kinetics of sorption of neptunium and found these reactions to be fast when the sorbing materials are tuff or clinoptilolite. When the solid was calcite or hematite, steady state had not been reached in 30 days of contact (experiment duration). It is suggested by Triay, et al. (1996a) that coprecipitation is the process that removes neptunium from solution when in contact with calcite. The NRC staff considers the coprecipitation process inappropriate for use in formulating a retardation factor from a K_d.

A comparison of batch tests and column tests for neptunium sorption (Triay, et al., 1996b) indicated that the batch sorption distribution coefficient could be used to predict arrival time. However, the elution curves showed dispersivity, which may suggest the isotherm is nonlinear, sorption is irreversible, or noninstantaneous. These column experiments did not involve significant calcite.

Batch sorption tests for plutonium failed to reach steady state in 32 days (experiment duration). Likewise, crushed tuff column experiments resulted in some of the plutonium eluting unretarded. Variation in the flow rate resulted in different proportions of the plutonium moving unretarded through the column. At fast flow rates, larger proportions moved unretarded; at slow flow rates, smaller proportions moved unretarded.

Triay, et al. (1997) states that "It is noteworthy that the experimentally determined redox behavior of plutonium in solution was quite distinct from the behavior predicted on the basis of EQ3 calculations (Nitsche, 1991)." The report goes on to say "the uncertainties in our

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knowledge of the solution behavior of plutonium will make it difficult to properly interpret the sorption behavior of that element." The NRC staff considers that this criterion has not been met for plutonium. Neither has the removal of plutonium from solution been shown to be the result of an ion exchange or adsorption reaction nor has the reaction been shown to be fast.

The crushed tuff column experiments for studying the elution of plutonium involved adding a pulse of plutonium-contaminated groundwater to the system and flushing through with uncontaminated groundwater. Some unknown reaction reduced the amount of plutonium exiting the column. It is possible that a precipitation reaction could have produced this result. If the experiments were performed with a continuous source instead of a pulse, the experiment might better simulate the situation expected at YM, where the plutonium source term should be continuous after the waste packages are breached.

Technetium has been eluted through crushed tuff columns at different flow rates. The flow rate did not affect breakthrough. The was little or no interaction with the solid as technetium moved through the column unretarded, so flow rates should have had no effect as observed.

5.1.1.5.3 CRITERION 2c3. Demonstrated Constant Bulk Chemistry

As discussed previously, an implicit assumption in using K_d to describe radionuclide sorption is that the chemistry of the groundwater is constant at the scale of discretization used in the transport model. Many of the sorption experiments discussed previously (e.g., Meijer, 1990) are performed using water from tuff aquifers in well J-13 in Jackass Flat and carbonate aquifers in well UE-25p#1. A number of studies, however, have demonstrated that water chemistry in the vicinity of Yucca Mountain can vary significantly with regard to parameters such as pH, ionic strength, and CO_3^{2-} concentration that may affect radionuclide retardation (Yang et al., 1996a,b; Perfect, et al., 1995; Turner, et al., 1999). Both DOE and NRC have made an effort to account for the effects of this changing chemistry in developing the PDFs used in TSPA-VA (Triay et al., 1997; Civilian Radioactive Waste Management System, Management and Operations, 1998a; U.S. Department of Energy, 1998c; Turner, et al., 1999). It also may be possible to demonstrate, through the use of process models, that the observed variability in geochemical conditions will produce minimal changes in K_d. Another approach is to simulate transport using a dynamic reactive transport system model (e.g., PHREEQC, MULTIFLO, HYDROGEOCHEM, etc.) to evaluate the effects of chemical heterogeneity on transport.

5.1.1.6 CRITERION 3a. Demonstrate That a Portion of the Flow Path Acts as an Isotropic Homogeneous Porous Medium [see USFIC IRSR (Nuclear Regulatory Commission, 1998b) on Deep Percolation]

Same as Criterion 2a.

5.1.1.7 CRITERION 3b. Demonstrated That Appropriate Values Are Used in Process Models

Process models have been applied to some extent to sorption of several radioelements of interest in PA including: neptunium, plutonium, uranium, americium, carbon, cesium, iodine, and selenium (Bradbury and Baeyens, 1993; Dzombak and Morel, 1990; Turner, 1995; Triay, et al., 1997; Paviet-Hartmann and Triay, 1997). These models typically use thermodynamic data for the radioelement of interest to calculate aqueous speciation, and to determine the amount of radioelement dissolved in solution and the amount sorbed onto the solid. This output can then be used to calculate K_d as a function of chemistry. Although process models can be applied over a wide set of geochemical conditions, it is recognized that determining the necessary model parameters relies on calibration against a set of well-constrained experiments. To provide additional confidence in the model results, the experiments used to calibrate the model should cover a range in critical parameters such as pH, ionic strength, and radionuclide concentration. The experimental variation in these parameters should span the range expected over the time period of interest at the scale of discretization in the PA abstraction.

5.1.1.8 CRITERION 3c. Demonstrated That the Three Implicit Assumptions (as in 2c) are Realized, If Process Models Are Intended to Yield a Constant K_d for Use in the Retardation Equation (Equation 1); Otherwise, Determined Transport in a Dynamic Reactive Transport System Model (e.g., PHREEQC, MULTIFLO, HYDROGEOCHEM, etc.)

Turner (1998) uses groundwater compositions from Perfect, et al. (1995) to suggest the possibility of a significant range of K_d values for neptunium and uranium for the YM region. However, the variation in groundwater composition in the portion of the pathway that is considered to be an isotropic homogeneous porous medium may be less than that over the whole region, which includes significant fractured rock. The limited availability of groundwater analyses for the porous rock units will likely result in a limited range of calculated K_d values. One additional concern stems from the evidence that in some wells, groundwater compositions have varied over time.

5.1.1.9 CRITERION 4. Where Data Are Not Reasonably or Practicably Obtained, Expert Judgement Has Been Used and Expert Elicitation Procedures Have Been Adequately Documented. If Used, Expert Elicitations Were Conducted and Documented in Accordance with the Guidance in NUREG-1563 (Nuclear Regulatory Commission, 1996) or Other Acceptable Approaches

The NRC staff considers K_d values from batch sorption tests, confirmed by crushed tuff column or other experiments, can be reasonably or practicably obtained. Consequently, expert elicitation would not appear to be appropriate, as a general matter, to use in place of experimentally determined sorption coefficients. This applies only to those radionuclides whose sorption characteristics affect performance.

5.1.1.10 CRITERION 5. Data and Models Have Been Collected, Developed, and Documented under Acceptable QA Procedures (e.g., Altman, et al., 1988), or If Data Were Not Collected under an Established QA Program, They Have Been Qualified under Appropriate QA Procedures

The Total System Performance Assessment—Viability Assessment (TSPA-VA) indicates that the K_d values for plutonium, uranium, and neptunium are Q-listed. All other K_ds and K_d distributions have not qualified (NQ) QA status.

5.1.2 Summary of the Status of Subissue 1

Most of the YM geochemical work in the past twenty years has been directed toward determining the retardation of radionuclides in porous rock. Significant progress has been made to address this subissue that is important to waste isolation and repository performance. However, in that time, there have been major changes in the conceptualization of the geologic setting of the repository that impact the relative importance of this subissue on performance. The major changes include the recognition that average infiltration is one or two orders of magnitude greater than original estimates, and the consideration of the point of compliance up to 20 km away from the repository. The greater average infiltration results in a greater proportion of the flux bypassing the sorptive porous rock by flow in fractures. A 20 km point of compliance would result in the need to consider the alluvium along with porous and fractured rock. These major changes reduce the relative importance of radionuclide transport in porous rock on PA.

As the foregoing discussion indicates, the NRC staff considers that the subissue has been met for certain radionuclides but not for others. Some of the radionuclides for which the subissue has not been resolved on the staff level may be important to performance.

The NRC staff finds that the approach adopted by LANL to determine minimum K_d values is logical and defensible. By performing batch sorption tests using site-specific materials, followed by confirmatory tests to establish the validity of the assumptions needed for the constant K_d approach, and then selecting the minimum K_d from all the tests, an acceptable value can be obtained.

In this summary, three radionuclides are chosen as examples to highlight successes and areas needing further work. They are neptunium, plutonium, and uranium. The minimum K_d approach has worked well for neptunium. The staff recognizes that multiple tests have been performed to establish reasonable K_d values for this radionuclide. Consequently, this subissue is met for neptunium. On the other hand, although both batch sorption tests and flow-through column tests have been performed to determine a minimum K_d for plutonium, significant inconsistencies have been observed. The NRC staff recognizes plutonium as problematic and encourages further work to establish defensible K_d values. For uranium, geochemical modeling suggests that a uranyl silicate phase, soddyite, could precipitate from solution, given the initial groundwater composition. Eliminating the possibility that processes other than sorption may be contributing to the removal of a radionuclide from solution is necessary for establishing a valid K_d. On the other hand, the thermodynamic modeling could be in error based on parameter uncertainties. To date, it does not appear that flow-through column tests were performed with uranium. Consequently, this subissue has not been resolved at the staff level.

5.2 STATUS OF SUBISSUE 2 RADIONUCLIDE TRANSPORT THROUGH ALLUVIUM

5.2.1 Criterion-By-Criterion Analysis

Same as Section 5.1.1.

5.2.2 Summary of the Status of Subissue 2

The status of this subissue is tied closely to that of the previous subissue. However, additional uncertainty is a result of the very limited information collected to date on the mineralogy, groundwater chemistry, and flow systems of the alluvium. Past efforts by the DOE have focused on characterizing the geologic media within 5 km of the repository because of the provisions of the then applicable 40 CFR Part 191. With the resultant increase in the length of the flowpath to the biosphere to 20 km, consistent with the proposed 10 CFR Part 63 (Nuclear Regulatory Commission, 1999c), a significant portion of relatively uncharacterized geologic media has been added to the system.

Although the NRC staff currently assumes in its TPA code that the alluvium acts as a homogeneous porous medium, it is recognized that little or no information is available to support that assumption. Furthermore, it is recognized that the staff's current assumption may be nonconservative.

The NRC staff expects that the series of boreholes to be drilled in the alluvium as part of the Nye County EWDP will provide significant information concerning its geologic, and hydrologic characteristics. It is expected that the mineralogy will reflect that used in batch sorption experiments for determining K_ds for radionuclides in tuff. If that is so, the laboratory work needed to address Subissue 1 will also address Subissue 2. Through early 1999, the EWDP had drilled eight wells to the south of YM. Lithologic logs available through the Nye County website (Nye County, 1999) indicate that much of the alluvium consists of valley fill deposits of gravel, silt, and sand varying in thickness from 33 m (110 ft) in well NC-EWDP-3S to more than 490 m (1618 ft) in well NC-EWDP-2D.

The determination of the modes of flow in the alluvium will be evaluated in the USFIC KTI (Nuclear Regulatory Commission, 1998b). If the alluvium is a composite of cut and fill structures resulting from the accretion of anastamosing channels, preferred pathways limiting water-rock interaction may result. If on the other hand, the alluvium is homogeneous, the application of experimentally determined K_ds to calculate retardation factors would be appropriate. Resolution of this subissue will await the geologic and hydrologic information to be collected by DOE.

5.3 STATUS OF SUBISSUE 3—RADIONUCLIDE TRANSPORT IN FRACTURED ROCK

5.3.1 Criterion-By-Criterion Analysis

For the most part, a criterion-by-criterion analysis of the status of Subissue 3 is the same as presented in Section 5.1.1. In current PA calculations (Nuclear Regulatory Commission, 1999a,b; U.S. Department of Energy, 1998c), no retardation is assumed in fractures in PA calculations, and radionuclides are transported through the fractures at the same velocity as groundwater. Under these conditions, Criteria 2 and 3 do not need to be satisfied, and flow issues related to fracture/matrix interaction and fracture flow velocity are the critical aspects of radionuclide transport. These flow issues are considered as part of the USFIC KTI, and the reader is referred to the USFIC IRSR (Nuclear Regulatory Commission, 1998b) for an analysis.

Criteria 4 and 5 are general in nature, and the status is the same as that listed in Sections 5.1.1.9 and 5.1.1.10.

5.3.2 Summary of the Status of Subissue 3

Experiments have been performed using fractured rock (Triay, et al., 1997). Whereas the retardation factor in fractures is typically assumed to be 1 (i.e., no sorption) in performance assessments, due to the uncertainty with regard to radionuclide transport T in fractured rock, preliminary experiments suggest that some retardation occurs. For example, neptunium experiments have been performed and show reduced recovery and a delay in the breakthrough relative to tritium and technetium. Field scale experiments (30 to 100 m) being conducted at the C-Wells complex (Reimus and Turin, 1997; Reimus, et al., 1998) result in bimodal breakthrough curves for nonreactive tracers (polyfluorinated benzoic acids, bromine), reactive solutes (lithium), and microspheres. Reimus, et al. (1998) suggest that fast pathways and diffusion from the fracture into the matrix may play a role in saturated zone transport (Reimus, et al., 1998). Resolution of this subissue will depend on a combination of laboratory experiments by DOE and continued tracer tests at the C-Wells and Busted Butte (Bussod and Turin, 1999) field sites.

5.4 STATUS OF SUBISSUE 4—NUCLEAR CRITICALITY IN THE FAR FIELD

Since publication of Revision 0 of the radionuclide transport IRSR, DOE made a major step toward resolution of the nuclear criticality subissue. The Disposal Criticality Analysis Methodology Report (U.S. Department of Energy, 1998d) was published, describing the process DOE will use to evaluate the potential for repository criticality as an input to TSPA. The DOE approach is to (i) identify physical and chemical configurations that have potential for leading to criticality, (ii) perform criticality analyses on each configuration to determine its potential for criticality according to a well-defined criterion, (iii) calculate criticality probabilities among those configurations exceeding the criterion, and (iv) estimate consequences for those configurations exceeding the probability criterion. The DOE report lists 11 specific "configuration classes" for the far field, detailing the scenario by which a particular configuration could conceivably lead to criticality. (The methodology report defines the "far field" as being external to the drift wall.) The scenarios involve transport of fissile material out of the drift in either solute or colloidal form, and accumulation in the far field. Accumulation mechanisms include precipitation due to geochemical processes (e.g., reduction), sorption, and colloid sorption or filtration.

NRC is initiating a review of the methodology report (U.S. Department of Energy, 1998d) that will result in a safety evaluation report (SER). Therefore, a detailed review of the far-field portions of the methodology report is not presented here. The methodology report does promise to provide a thorough assessment of far field criticality potential and may lead to resolution of this subissue. This approach is in general consistent with the acceptance criteria presented in this IRSR.

5.4.1 Criterion-by-Criterion Analysis

5.4.1.1 Criterion Set 1

The first set of acceptance criteria in Section 4.4.1 deals with the validity of data and models, and the level of conservatism, used in the far field criticality assessment. The NRC review of the DOE methodology report (U.S. Department of Energy, 1998d) will resolve any deficiencies in these areas. A particular focus of the NRC review is expected to be on validation of geochemical models for U and Pu transport and re-deposition.

5.4.1.2 Criterion Set 2

The second set of acceptance criteria in Section 4.4.1 is concerned with DOE's far field criticality consequence analyses. The NRC review of the DOE methodology report (U.S. Department of Energy, 1998d) will resolve any deficiencies in these areas. A particular focus of the NRC review is expected to be on whether DOE establishes reasonable assurance that inventory increases and thermal pulses due to far field criticality will negligibly impact repository performance.

5.4.1.3 Criterion Set 3

The third set of acceptance criteria in Section 4.4.1 is concerned with DOE's assessment of the probability of criticality in far field configurations. The NRC review of the DOE methodology report (U.S. Department of Energy, 1998d) will identify any deficiencies in these areas. The NRC staff will interact with the DOE to resolve issues that are identified during the review. A particular focus of the NRC review is expected to be on screening criteria.

5.4.2 Far Field Criticality in the Viability Assessment

In the VA and supporting TSPA-VA, nuclear criticality is treated as one of four disruptive processes (U.S. Department of Energy, 1998c; Civilian Radioactive Waste Management System, Management and Operations, 1998a) a simplified analysis was described. The effects of external criticality on performance are discussed in Volume 3, Section 4.4 of the VA (U.S. Department of Energy, 1998c). Consistent with the proposed methodology (U.S. Department of Energy, 1998d), the DOE first evaluated the likelihood of criticality and then assessed its impact on repository performance (U.S. Department of Energy, 1998c). The VA describes two external criticality mechanisms—one near-field and one far field—and concludes on the basis of a more detailed discussion in the TSPA-VA technical basis report (Civilian Radioactive Waste Management System, Management and Operations, 1998a) that they are exceedingly unlikely. The far field scenario discussed depends on transport of U to the far field followed by deposition due to locally reducing conditions. It is concluded (Civilian Radioactive Waste Management System, Management and Operations, 1998a) that this scenario is highly unlikely due, in addition to the insufficiency of U mass concentration, to the absence in the transport pathway at YM of geochemical subsystems providing appropriately reducing conditions.

The consequences of an external criticality for performance are discussed only briefly in the VA and TSPA-VA Technical Basis Report (U.S. Department of Energy, 1998c, Civilian Waste Management System, Management and Operations, 1998a) and only in terms of the resulting increase in radionuclide inventory. An example analysis from an earlier report (Civilian Radioactive Waste Management System, Management and Operations, 1998b) of a single critical event in fractured tuff showed an increase in radioactivity in the reactor of only 14 percent, with the excess decaying to 3 percent after 20,000 yr. Due to a combination of the low probability of the event and the negligible effect on radionuclide inventory, the VA concludes that external criticality has no impact on repository performance.

The VA treatment of external criticality is preliminary and incomplete but, as discussed above, the methodology report suggests that future criticality analyses will be systematic and comprehensive. A particular lacking in the VA is in consideration of heat input effects. An external criticality, particularly in the near field, may result in a minor thermal pulse. Coupled processes could in turn provide positive or negative feedback to the transport process responsible for the critical configuration. This interaction between criticality and coupled processes should be considered in future scenario analyses.

In addition to the proposed criticality analysis methodology, the DOE in Volume 4 of the VA (U.S. Department of Energy, 1998c) lists future and ongoing investigations that will improve their ability to evaluate the external criticality issue. These technical investigations are focused on colloid formation, stability, and transport, because colloids are viewed as a potential means for transport of Pu out of the WP.

5.4.3 Summary of the Status of Subissue 4

In summary, based on previous work DOE's work in the viability assessment (U.S. Department of Energy, 1998c), the four step process DOE will use to evaluate the potential for repository criticality, and the consequences DOE will investigate (U.S. Department of Energy, 1998d), NRC staff believes DOE is on a path to resolution of this subissue and has no further questions concerning potential nuclear criticality in the far field. This subissue is resolved at the staff level. The NRC will continue to review DOE's Disposal Criticality Analysis Methodology Report and will evaluate DOE's analysis supporting their screening of disposal criticality in the far field as part of the safety evaluation report process.

5.5 STATUS OF OPEN ITEMS

The NRC has raised concerns about the DOE Site Characterization and PA programs in areas related to radionuclide transport. These concerns have been expressed in the following:

> Staff Site Characterization Analysis (SCA) of the Department of Energy's Site Characterization Plan, Yucca Mountain Site, Nevada (Nuclear Regulatory Commission, 1989)

The NRC review of the DOE SCP (Nuclear Regulatory Commission, 1989) resulted in ten comments relating to radionuclide transport. DOE responded to those comments and based on those responses the NRC staff considered six of the comments resolved (Letter from R. Bernero to J. Bartlett, dated July 31, 1991). The resolved comments are SCA Comments 23, 26, 27, 28, 29, and 30. Since then, DOE has adopted a revised program plan (U.S. Department of Energy, 1996) and the RSS that refocuses efforts to address issues relating to the waste containment and isolation. Consequently, study plans described in the

SCP have changed in scope, been deferred or canceled. However, the NRC staff will continue to track progress made toward resolution of those concerns that remain unresolved. The status of the unresolved SCA comments are discussed below.

SCA: **Comment 24** (Nuclear Regulatory Commission, 1989; Page 4-29). Standard solubility approaches alone are not sufficient for determining reliable thermodynamic properties of zeolites.

Status: ***Closed***

Basis: This comment relates indirectly to subissues concerning radionuclide transport in porous rock and fractured rock where zeolites are expected (Subissues 1 and 3). Zeolites are considered strong sorbers of some significant radionuclides. Consequently, the stability of these phases is important to radionuclide mobility. Alteration of zeolites can lead to less sorptive assemblages consisting of albite and analcime. This comment relates directly to the four subissues of ENFE KTI dealing with coupled processes. Based on a study by Hemingway and Robie (1984), which described problems with gleaning thermodynamic information for zeolites from solubility studies, the NRC staff was concerned that proposed plan to determine the end-member free energies for clinoptilolite-heulandite may be inadequate. Hemingway and Robie (1984) recommended "...the best estimates of the thermodynamic properties of zeolites will be obtained from simultaneous analysis of synthesis and stability data, calorimetric data, and various metastable equilibrium measurements, each of which will place limits upon one or more of the thermodynamic properties of a given zeolite phase." The Summary and Synthesis Report on Mineralogy and Petrology Studies for the Yucca Mountain Site Characterization Project, Volume III Kinetics and Thermodynamic of Mineral Evolution at Yucca Mountain describes multiple techniques used to estimate thermodynamic data for clinoptilolite, analcime, mordenite. These techniques include solubility studies, thermogravimetric studies, calorimetry and modeling. Furthermore, a discussion of uncertainties provides for reasonable bounds to which the thermodynamic models can extend. The NRC staff recognizes that significant progress has been made to address the thermodynamic properties of the zeolites. The tremendous compositional variability of zeolites at YM makes the task of predicting mineral stability under the various conditions expected at the YM repository difficult. Since multiple techniques have been used to determine the thermodynamic parameters of zeolites, the NRC staff considers this comment resolved.

SCA: **Comment 31** (Nuclear Regulatory Commission, 1989; Page 4-34). The determination of some parameters and conditions, such as speciation, kinetics, and matrix diffusion under fracture-flow conditions, are not planned.

Status: ***Closed***

Basis: This comment relates to the subissue on radionuclide transport in fractured rock (Subissue 3). At the time of the comment, the NRC staff was concerned that the chemical environment within fractures may be different from those in the matrix. As a consequence, comparisons of the results of batch sorption experiments and the fracture flow experiments might be misleading or ambiguous. Subsequent studies have shown

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that fracture mineralogy can be different from that in the matrix (Carlos, et al., 1995) and fracture water may be different from matrix water (Yang, et al., 1996a). To address this concern, fracture mineralogy of solid rock core to be used in fracture-flow experiments was determined and used in batch sorption tests (Triay, et al., 1997). The fracture flow experiments involved neptunium, technetium, and tritium. Results of these experiments indicated that processes and conditions existed to retard the transport of neptunium. The processes proposed could include sorption within the fracture or matrix diffusion or both. The significance of these experiments was to demonstrate that assumptions often used in performance assessments that radionuclides move unretarded in fractures is too conservative. The NRC staff recognizes that assuming no retardation in fractures may be conservative but have not yet seen information that could be used to quantify radionuclide transport in fractured rock on scales appropriate for modeling the YM repository.

Some questions remain concerning the fracture-flow experiments. Table 3.2 of Triay, et al. (1997) indicates that fracture aperture and porosity are still to be determined. The fact that these experiments led to incomplete recovery suggests further work to determine where the radionuclides now reside. Furthermore, the report does not provide information concerning the mass of radionuclide added to the column. Mass balance considerations are needed to explain the transport of radionuclide through the fractured rock.

With regard to reference to matrix diffusion in Comment 31, the NRC staff recognizes that experiments done in the C-Wells where tracers with different diffusivities suggest processes that could be ascribed to matrix diffusion. There are other possible explanations for the outcome of these tests.

The NRC staff considers that remaining concerns related to radionuclide transport in fractured rock are covered in the acceptance criteria of Subissue 3. Consequently, Comment 31 will be closed as a separate issue, and the NRC staff will track progress in resolving Subissue 3 related to radionuclide transport in fractured rock.

SCA: **Comment 96** (Nuclear Regulatory Commission, 1989; Page 4-76). The investigations to characterize radionuclide retardation are focused on the determination of a K_d for use in the equations $R_{f,matrix} = 1 + \rho_{b,matrix}K_d/\theta_{matrix}$ and $R_{f,fracture} = 1 + \rho_{b,fracture}K_d/\theta_{fracture}$, Equations 8.3.5.13-14a and b. It has not been demonstrated in the SCP that the use of these equations to model the complex heterogeneous medium of YM is valid for all expected (i.e., anticipated) states of the natural flow system (i.e., full range of unsaturated and saturated).

Status: ***Open***

Basis: Comment 96 relates to all three subissues of this KTI that refer to radionuclide transport. It is noted that the comment incorrectly uses ρ_f, and K_d in Equation 8.3.5.13-14b instead of σ_f, the fracture surface area per unit volume of rock and K_A, a distribution coefficient for the radionuclide species on a per unit surface-area basis. This error, however, does not affect the major issues raised in the comment. These concerns included assumptions that must be present for the equations to be valid. For example, constant chemistry is required for appropriate use of these equations. Recent preliminary site characterization activities suggest chemistries may vary over short distances (White paper on Eh-pH conditions in wells WT-17 and WT-3). Variations in bulk groundwater chemistry can lead to excursions in radionuclide concentrations (e.g., Fuentes, et al., 1987).

These equations are used in PAs to describe the relative rate of transport of radionuclides to the flow rate of groundwater (average linear velocity). These equations do not involve concentrations of radionuclides that are currently considered to be important to repository safety (e.g., RSS).

The SCP states that "...because fracture surface areas are usually much smaller than pore surface areas and because chemical equilibrium may not be reached in rapid fracture flows, the adsorptive retardation in fracture flow R_f can be regarded as a number of the order of unity (Sinnock, et al., 1984) (i.e., sorption in fractures may be ignored)."

With the observations of ^{36}Cl and ^{3}H in the deep subsurface, fracture-flow conditions have attracted heightened attention. Progress will be tracked by the NRC staff. This comment is considered to be open. Tests like those being conducted at the Busted Butte may provide information to suggest appropriate method to represent radionuclide transport in fractured and porous rock.

SCA: **Comment 109** (Nuclear Regulatory Commission, 1989; Page 4-85). Coupling times for the transfer of mass (radionuclides) between matrix and fracture flow is repeatedly cited as a key factor in determining the appropriate model for radionuclide transport at YM, yet alternative models depending on the nature of the coupling do not appear to be treated in the hypothesis testing tables.

Status: ***Open***

Basis: This comment relates to the subissue on radionuclide transport in fractured rock. The interaction between fracture and matrix is an extremely important aspect of radionuclide transport. Where PAs assume no "adsorptive" retardation in the fracture, the capability for radionuclides to move into the matrix provides retardation in a fracture-flow situation. This process can involve advection or diffusion into the matrix or stagnant portions of the fracture network. The staff questioned how fracture-matrix coupling constants, determined from laboratory experiments on fractured core, would be used on the spatial and temporal scales appropriate for modeling the performance of the YM repository. Studies at the C-well complex for the SZ and Busted Butte for the UZ may expand the scale to which these effects apply. Whether these tests will provide information on the appropriate scale is unknown at this time.

The staff raised the concern that fracture lining materials may impede transfer between the fracture and the matrix. LANL experiments (ref) show that fracture lining materials are as permeable as the matrix. Thus, it is suggested that fracture lining materials do not impede the transfer. On the other hand, a non site-specific study (Robinson, et al., 1998) suggest that fracture skins should be considered in transport analyses.

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Evidence concerning the interaction between fracture and matrix is apparently conflicting. The fractured rock experiments (Triay, et al., 1997) suggest some process is occurring to retard the radionuclides. This could be sorption on fracture lining minerals or matrix diffusion or both. Several sources of hydrochemical data suggest interactions between the fracture fluid and the matrix fluids are limited. For example, perched water, which is assumed to represent fracture water, and pore water at the same depth in UZ#14 have chloride concentrations of 6-15 mg/L and 87.5 mg/L, respectively (Yang, et al., 1996a,b). Also, in the SZ, some units that contain calcite in the matrix are undersaturated with respect to calcite in the fracture water.

In the July 6,1998, letter from M. Bell to S. Brocoum on NRC Comments on the DOE TSPA, the staff's concern about the transfer term for fracture-matrix exchange is expressed. Estimation of this term is uncertain. Consequently, the staff considers this comment open.

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A.1 APPENDIX A

A.1.1 MATRIX MINERALOGY

General descriptions of individual aquifers and confining units in the YM vicinity are discussed in detail in several studies (Luckey, et al., 1996; Czarnecki, et al., 1997; Hinds, et al., 1997). A summary of these investigations is provided in the USFIC IRSR (Nuclear Regulatory Commission, 1998b). Details on mineralogy in the aquifer are provided below.

At Yucca Mountain, host rocks are silicic tuffs [70 to 80 percent SiO_2 (Byers, 1985)]. These rocks are variably vitric, devitrified to an assemblage of silica minerals and alkali feldspar, or altered primarily to the silica-rich zeolites, clinoptilolite and mordenite, or to analcime at depth (Bish and Chipera, 1989). Glass alteration in the Calico Hills formation below the repository horizon is accompanied by incongruent precipitation of mordenite and clinoptilolite, zeolites with important sorptive characteristics (Ames, 1964; Murphy and Pabalan, 1994; Bertetti, et al., 1998; Pabalan, et al., 1998). In the proposed repository horizon at Yucca Mountain, the tuffs are devitrified to alkali feldspar and silica mineral polymorphs (cristobalite, quartz, and tridymite) (Bish and Chipera, 1989). Here, smectite is the dominant aluminosilicate alteration phase, occurring in abundances up to five percent (Bish, 1988). In lower volcanic units at Yucca Mountain, primary glass has been altered to analcime ±kaolinite rather than clinoptilolite. This mineralogic change, which is associated with the disappearance of cristobalite with depth, is consistent with a decrease in the activity of aqueous silica (Kerrisk, 1983).

The volcanic rocks at Yucca Mountain are rhyolitic, zoning upward to quartz latitic in composition, rich in silica, alumina, and alkali metals (Lipman, et al., 1966). The bulk composition of unaltered rocks can be reasonably approximated (to greater than 97 percent) by two components, approximately one mole of alkali feldspar with the composition $Or_{53}Ab_{45}An_2$ and two moles of a silica phase.

Mineralogical characterization of the rocks (Bish and Chipera, 1989) and petrographic interpretation (Broxton, et al., 1987) reveal general patterns of mineral occurrences. Margins of individual volcanic units were quenched to glass on eruption, while the insulated flow interiors mostly devitrified. Subsequently, glassy units have been partially-to-completely altered to secondary minerals. Four vertically disposed diagenetic zones have been described at Yucca Mountain based on the degree and nature of alteration (Smyth, 1982; Broxton, et al., 1987). The top zone (Zone I) retains unaltered glass with minor clay minerals, zeolites, and opal. In Zone II, glass is completely replaced by clinoptilolite and sometimes mordenite with lesser opal, potassium feldspar, clay, and quartz. In Zone III, the alteration assemblage is dominated by analcime with lesser potassium feldspar and quartz, and minor calcite and clay. Zone IV, which occurs in the lowest members of the volcanic strata, contains the mineralogy of Zone III but with analcime replaced by albite. Data from Bish and Chipera (1989) indicate that cristobalite is generally abundant in devitrified rocks associated with diagenetic Zones I and II, but is absent in the lower zones. Conversely, kaolinite occurs only below the mineralogic discontinuity between Zones II and III.

Zone II of Broxton, et al. (1987) generally straddles the water table at Yucca Mountain and largely occupies a position between the proposed repository horizon and the water table. The geochemical characteristics and evolution of this zone are of particular significance because it occurs along a path of possible radionuclide migration. Zeolite minerals, notably clinoptilolite, the dominant alteration mineral in Zone II, are widely cited as a favorable condition for radioactive waste disposal at the Yucca Mountain site because of their high ion exchange and adsorptive capacities (U.S. Department of Energy, 1988). It is also likely that, as the first alteration product of volcanic glass, zeolites would play an important role in controlling groundwater chemistry that may interact with engineered repository components or released radionuclides.

Broxton, et al. (1986) report extensive chemical analytical data for clinoptilolites from Yucca Mountain determined by microprobe analyses. In general, clinoptilolites are relatively rich in silica (Si/Al = 4 to 5 on an atomic basis) and have a wide variety of alkali and alkaline earth contents, which are generally correlated with their geographic distribution (Broxton, et al., 1986, 1987). Clinoptilolites near the surface from Zone I are rich in calcium (and magnesium). In Zones II and III, clinoptilolites tend to vary from sodium and potassium rich varieties in the west to calcium (and magnesium) varieties in the east. In potassium-rich rocks in the northern part of Yucca Mountain, clinoptilolites are rich in potassium, but also trend from relatively calcium- (and magnesium-) rich varieties nearer the ground surface to potassium-rich varieties at depth.

Clay minerals tend to occur in all stratigraphic and diagenetic zones, but in relatively small quantities. Based on X-ray diffraction (XRD) data, clay minerals in rocks above the water table at Yucca Mountain are randomly interstratified illite/smectite with less than 25 percent illite (Bish, 1989). The potassium content and the illite fraction of the interstratified clays tend to increase with depth. However, in the unsaturated zone, the sodium and calcium components of the smectites predominate (Bish, 1989).

Calcite also occurs locally both above and below the water table at Yucca Mountain and is prevalent in caliche near the ground surface and in fracture fillings. It is generally the most recently precipitated mineral at Yucca Mountain, with sample ages predominantly between 26,000 and 310,000 yr (Szabo and Kyser, 1990). Stable isotope and trace element compositions of calcites generally denote a distinction between those below the water table and those above it (Whelan and Stuckless, 1992; Vaniman, 1993). Unsaturated zone calcites generally have chemical characteristics similar to those in soil-zone caliche at Yucca Mountain (Whelan and Stuckless, 1992).

Mineral abundances for hydrostratigraphic units at Yucca Mountain have been determined using quantitative XRD and summarized in the synthesis report on mineralogy and petrology studies (Vaniman, et al., 1996a; Volume 1, Section 2). Mineralogy has been determined for cores from 21 different wells drilled in the vicinity of Yucca Mountain. Figure A-1 summarizes the mineral abundances in drillholes USW G-4 and UE-25 UZ#16. Table A-1 summarizes the depth to water and the thicknesses of the stratigraphic units.

In both USW G-4 and UE-25 UZ#16, the top volcanic unit is the Tiva Canyon Tuff. Mineralogy in the Tiva Canyon is dominantly cristobalite and alkali feldspar. A thin basal vitrophyre is dominated by glass, with minor feldspar and cristobalite. Beneath the Tiva Canyon lie the Yucca Mountain and Pah Canyon Tuffs (USW G-4) and Paintbrush bedded tuff (UE-25 UZ#16).

Thin layers rich in clay minerals and smectite have apparently formed at the expense of feldspar and/or glass immediately above and within the vitrophyres, suggesting that focused flow along the vitrophyre interface has led to increased alteration.

Within the repository block, the Topopah Spring Tuff is about 300–350 m thick and the mineralogy is dominated by alkali feldspar (overall average composition of $Or_{50}Ab_{42}An_8$) and silica polymorphs (tridymite, α-cristobalite, quartz). Based on mineral abundance, the Topopah Spring Tuff can be broadly divided into four units, including an upper vitrophyre that is almost entirely glass. Beneath the upper vitrophyre, the tuff is devitrified with alkali feldspar increasing quickly with depth. About the upper one-fourth of the Topopah Spring Tuff is a crystal-rich quartz latite. The lower three-fourths of the Topopah Spring Tuff, including the proposed repository level, is a crystal-poor rhyolitic tuff. A vitrophyre about 10–40 m thick is at the base. Alkali feldspar ($\sim Or_{47}Ab_{44}An_9$) abundance in the upper 60–80 m of quartz latite is high (70–80 weight percent). For roughly the lower 250–300 m in the rhyolitic tuff, feldspar ($\sim Or_{58}Ab_{36}An_6$) abundance is fairly constant at about 55–65 weight percent. There is significant heterogeneity in the abundance of individual silica polymorphs over narrow sampling intervals in the Topopah Spring Tuff. The total weight percent silica (tridymite + cristobalite + quartz + opal-CT), however, is relatively constant, at 30 to 40 percent in the rhyolitic tuff of the Topopah Spring. Total silica polymorph abundance decreases sharply in the quartz latite cap and immediately above and within the basal vitrophyre. Thin clay-rich layers form immediately above the basal vitrophyre, again suggesting flow along the vitrophyre interface.

Below the basal vitrophyre and in the upper part of the Calico Hills Formation, clinoptilolite increases markedly. Clinoptilolite abundance of as much as 80 percent occurs over thin intervals, with significant thicknesses of 55 to 60 weight percent. Clinoptilolite seems to form at the expense of glass, with increasing clinoptilolite mirrored by decreases in glass and feldspar abundance. Heterogeneity is still pronounced, particularly in the silica polymorphs. In USW G-4, cristobalite (including opal-CT) is the dominant silica polymorph, whereas, in UE-25 UZ#16, quartz, and opal-CT occur in subequal amounts. Total silica polymorph abundance does not vary as much as individual polymorph abundance, and is less than in the devitrified part of the Topopah Spring (about 25 percent versus 35 percent, respectively). Beneath the Calico Hills Formation, the Prow Pass tuff down to the water table is almost completely quartz and alkali feldspar (about 40 and 55 weight percent, respectively), with minor smectite.

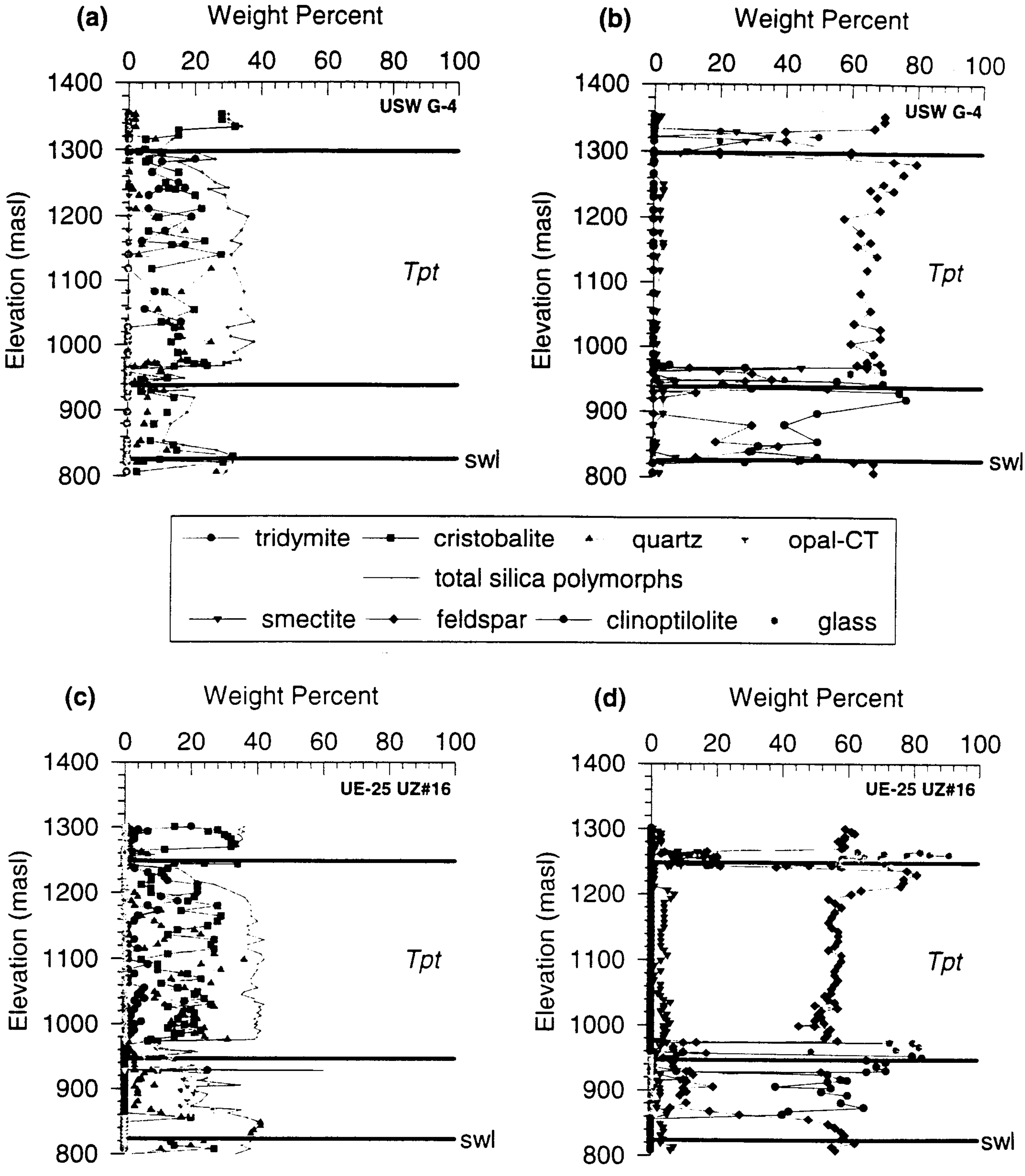

Figure A-1. Mineralogy variations with well depth. (a) silica polymorphs in USW G-4; (b) aluminosilicate minerals and glass in USW G-4; (c) silica polymorphs in UE-25 UZ#16; (d) aluminosilicate minerals and glass in UE-25 UZ#16 (from Vaniman et al., 1996a)

Table A-1. Unit thickness in wells USW G-4 and UE-25 UZ#16

Unit	USW G-4 depth (m)	USW G-4 elevation (masl)	UE-25 UZ#16 depth (m)	UE-25 UZ#16 elevation (masl)
Alluvial Fill	—	—	0–12.1	1312.7–1300.6
Tiva Canyon Tuff	9.1–45.1	1358.0–1322.0	12.1–49.0	1300.6–1263.7
Yucca Mountain Tuff	45.1–51.3	1322.0–1315.8	—	—
Pah Canyon Tuff	51.3–69.5	1315.8–1297.6	—	—
Paintbrush Bedded Tuffs	—	—	49.0–63.9	1263.7–1248.8
Topopah Spring Tuff (Tpt)	69.5–428.7	1297.6–938.4	63.9–366.2	1248.8–946.5
Calico Hills Formation	428.7–519.8	938.4–847.3	366.2–443.6	946.5–869.1
Pre-Ta bedded tuffs	519.8–537.3	847.3–829.8	443.6–452.6	869.1–860.1
Prow Pass Tuff	537.3–681.7	829.8–685.4	452.6–513.3[a]	860.1–799.4
Bullfrog Tuff	681.7–836.1	685.4–531.0	—	—
Tram Tuff	836.1–914.4[a]	531.0–452.7	—	—
SWL	541.3	825.8	489.2	823.5

[a] Total depth: USW G-4 = 914.4 m; UE-25 UZ#16 = 513.3 m

B.1 APPENDIX B

B.1.1 UNSATURATED ZONE WATER CHEMISTRY

B. 1.1.1 Major Element Chemistry

Porewater chemistry at Yucca Mountain is based on a relatively small set of analyses (Figure B-1). The samples are collected by uniaxial and triaxial compression (Yang, et al., 1996a,b) or ultracentrifugation (Fabryka-Martin, et al., 1997) of preserved cores, and are limited to those samples from which enough water can be extracted for analysis. For this reason, most of the samples are limited to Pah Canyon nonwelded tuffs, bedded tuff, or the Calico Hills and Prow Pass formations, due to higher moisture contents by weight (Yang, et al., 1996a). There are no samples available from the repository horizon, but some samples in UE-25 UZ#5 and USW NRG-6 were collected from samples taken near the top of the Topopah Spring Tuff. In most cases, TDS are greater in the unsaturated zone porewater than in the saturated zone tuffaceous groundwater (Yang, et al., 1996a). Most of the unsaturated zone porewater is of a calcium-sulfate or calcium-chloride type, as opposed to the sodium-bicarbonate waters typical of the tuffaceous saturated zone aquifers. There is also some suggestion in the geochemical data that water has flowed relatively quickly along fractures (similar chemistry for samples collected at two different levels), and laterally through tilted porous tuffs rather than along lithologic contacts (Yang, et al., 1996a). Waters attributed to fracture flow in the unsaturated zone at Rainier Mesa (White, et al., 1980) are typically more dilute than interstitial porewaters, particularly with regard to chloride and sulfate (Murphy and Pabalan, 1994). In general, chloride decreases with depth, suggesting greater evaporation of porewater closer to the surface (Murphy and Pabalan, 1994). The chloride profile may also be consistent with a conceptual model of deep circulation with episodic flow (Fabryka-Martin, et al., 1996).

B.1.1.2 Stable Isotope Chemistry (δD, δ^{18}O, and δ^{13}C)

Deuterium and ^{18}O of unsaturated zone porewaters decrease gradually with depth through the upper two-thirds of the Topopah Spring Tuff (Yang, et al., 1996b). For example, in porewaters collected from the bedded tuffs above the Pah Canyon Tuff, deuterium ranges from about −88 to −105‰ and δ^{18}O from −12.4 to −14.3‰ relative to Standard Mean Ocean Water (SMOW). In porewater from the Topopah Spring Tuff, deuterium ranges from about −95 to −105‰ and δ^{18}O from about −13.0 to −14.8‰. The isotopic composition of the porewater vicinity, suggesting that recharge by local precipitation occurs during the winter months.

Deuterium and ^{18}O content depend on mineralogy and on the extraction technique used. Waters collected by vacuum distillation from zeolitized units such as the Calico Hills Formation, Prow Pass Tuff, and Bullfrog Tuffs, are more depleted in deuterium and ^{18}O than those distilled from the Topopah Spring Tuff and Pah Canyon Tuff (Yang, et al., 1996b). Much of the depletion observed in water from zeolitized units disappears when water is collected using a compression technique (Yang, et al., 1996b). For example, water extracted by distillation from high zeolite content in the Calico Hills nonwelded unit includes a mix of pore water and zeolite channel water, and is depleted in deuterium and ^{18}O, with δD of about −120‰ and δ^{18}O of −17.9‰ SMOW; water collected by triaxial compression ranges in δD from −98 to −103‰ and

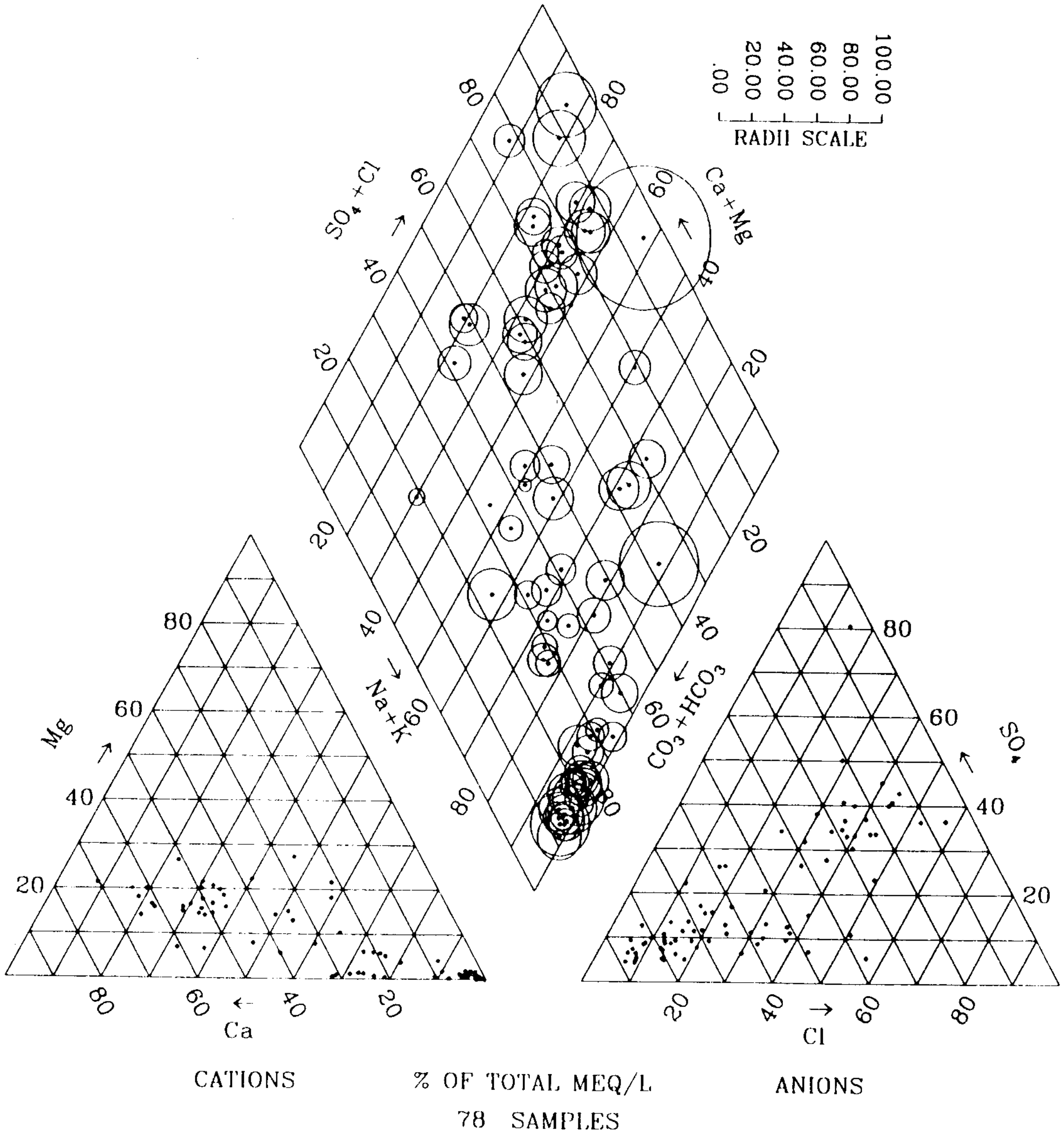

Figure B-1. Unsaturated zone porewater chemistry in meq/L. Circle diameter represents total dissolved solid concentration (from Yang, et al., 1996a).

$\delta^{18}O$ from -12.5 to -13.7‰ SMOW, similar to the range observed in the nonzeolitized Topopah Spring Tuff. Variation in $\delta^{13}C$ reported for USW UZ#14 is broader [-10.3 to -25.0‰ relative to the Pee Dee Belemnite (PDB)] for the unsaturated zone porewaters than those observed for perched water or saturated zone waters (Yang, et al., 1996a). The total range is similar to that reported for soil CO_2 at the Nevada Test Site (NTS). Three water samples taken from the upper part of the Topopah Spring Tuff, the bedded tuff immediately above the Topopah Spring Tuff, and the contact between the bedded tuff and the overlying Tiva Canyon (UE-25 UZ#16) exhibit a narrower range in $\delta^{13}C$ of -9.0 to -9.4‰ PDB. The narrower range suggests dissolution of caliche at the shallower depths, but the small number of samples makes this somewhat uncertain. Deeper samples from the Calico Hills formation taken in the same borehole show a much broader range in $\delta^{13}C$, from -10.3 to -23.3‰ PDB, suggesting both a biological CO_2 gas component and zones for preferential flow as opposed to a well-mixed water (Yang, et al., 1996a).

B.1.1.3 Radiogenic Isotopes

Tritium is typically low in the unsaturated zone porewaters, at or below 10 T.U. There are some peaks in the Pah Canyon and bedded tuff immediately above the Topopah Spring Tuff. Additional spikes of 20 to 40 T.U. are found above the basal vitrophyre in the Topopah Spring Tuff (UE-25 UZ#16), and spikes as high as 100 T.U. are found in the Calico Hills Formation (UE-25 UZ#16). Similar profiles have been observed for ^{14}C (Yang, et al., 1988, 1996a) and ^{36}Cl (Liu, et al., 1995). For example, in USW UZ#14 and UE-25 UZ#16, ^{14}C concentrations ranging from 53 to 97 pmc (percent modern carbon) were reported for samples from the Calico Hills Formation (Yang, et al., 1996a). Because these samples are taken from matrix pore water rather than sampling along large through-going fractures, it also suggests that there is either some imbibition into the matrix or there are microfractures being sampled in the triaxial compression.

B.1.2 SATURATED ZONE WATER CHEMISTRY

B.1.2.1 Major Element Chemistry

Based on major element analyses of well and spring waters, Schoff and Moore (1964) identified three types of waters in the NTS vicinity:

(i) Na+K waters that the authors related to tuff aquifers or samples collected from tuffaceous alluvium. For these waters, the authors used an operational definition where Na+K makes up 60 percent or more of total cations in equivalents. In all cases, Na is the dominant cation, with only small amounts of K.

(ii) Ca+Mg waters related to carbonate aquifers and carbonate-bearing alluvium. As with Na+K waters, the authors developed an operational classification such that Ca+Mg makes up more than 60 percent of the total cations in equivalents. Unlike the Na+K waters, either Ca or Mg can be the dominant cation, and they are typically present in subequal amounts.

(iii) Mixed types where neither cation pair constitutes more than 60 percent of total cations, but each pair amounts to more than 40 percent. These waters were found predominantly in carbonate rocks, with some occurrence in alluvium. Schoff and Moore (1964) observed that either cation pair might predominate.

Claassen (1985) contoured major element hydrochemistry south of Yucca Mountain and identified a southeast trending trough of low concentrations centered beneath the main drainage emerging from Fortymile Canyon into the central Amargosa Desert. Higher concentrations are associated with readily dissolved playa deposits, and lower TDS are associated with coarser, more permeable deposits. Relative to the more dilute groundwaters in the trough, higher ionic concentrations (e.g., Na^+, Ca^{2+}) were measured for groundwater samples collected from the upstream reaches of the Amargosa River channel. Further downstream, below the confluence of the Fortymile Canyon and Amargosa River drainages, concentrations decrease again, suggesting a mixing (and dilution) of the two waters. The high Na^+ of Amargosa River groundwater samples from the upstream reaches suggest interaction with tuffaceous alluvium, while the elevated Ca^{2+} may be due either to mixing of alluvial waters with upwelling water from the underlying carbonate aquifers, or to interaction with carbonate alluvium at the base of the Funeral Mountains. Silica activity may buffer mineral dissolution and secondary mineral precipitation. Silica activities in the Yucca Mountain vicinity and Oasis Valley are relatively constant at 10^{-3}, between saturation with cristobalite and amorphous silica (Murphy and Pabalan, 1994).

Across the concentration gradient at the west side of the trough in west-central Amargosa Desert, Claassen (1985) noted east-west trends of decreasing Ca/Na in groundwaters from the tuffaceous alluvium. Because the potentiometric contours indicate a southerly flow, Claassen (1985) considered it unlikely that significant east-west mixing of fluids occurred; this is supported by the lack of significant changes in Cl^- concentration across the gradient. Groundwater diffusion with calcite precipitation to reduce Ca^{2+} was also considered to be inadequate by Claassen (1985), due to a lack of a corresponding decrease in calcite saturation. Claassen (1985) suggested that the observed trend was more likely to be due to continued evolution of the valley-fill water by interaction with tuffaceous alluvium and increased precipitation of clinoptilolite, but offered no mineralogical evidence to support this hypothesis.

Across the gradient on the east side of the trough, Schoff and Moore (1964) used increasing Ca/Na ratios in east-central Amargosa Desert towards the Spring Mountains to indicate mixing between $Na^+ + K^+ + HCO_3^-$ tuffaceous waters from the north and $Ca^{2+} + Mg^{2+} + HCO_3^-$ groundwaters recharged in the carbonates in the Spring Mountains. Based on major ion hydrochemistry and a change in the potentiometric contours, Claassen (1985) proposed mixing across a region 5 to 10 km northeast of the Ash Meadows discharge zone. This region, west of Rock Valley Wash, occurs near the intersection of the Specter Range Thrust Fault and the Gravity Fault, and may represent a break in the hydrologic barrier separating the Ash Meadows spring line from the Amargosa Desert. Hydrochemical and temperature data (i.e., higher temperatures in the deeper carbonate waters) support upwelling and mixing of carbonate waters with groundwaters in valley fill. Using major element chemistry and presumably conserved ions such as Cl^-, Claassen (1985) was able to show that progressive mixing of dilute waters from the center of the trough with mixed valley fill carbonate waters leaking across the Gravity Fault/Specter Thrust intersection could produce the observed hydrochemistry. Waters closer to the intersection were comprised of a larger component of carbonate water, while there is a rough increase in the tuff waters component from north to south. A comprehensive compilation of regional saturated zone groundwater chemistry is presented by Perfect, et al.

(1995). A subset of these analyses from the Yucca Mountain vicinity is presented in Figure B-2.

There is some evidence of vertical chemical zoning in saturated zone waters. For example, periodic downhole monitoring of Eh in well WT-17 indicates that Eh varies from oxidizing (> 250 millivolts) to reducing (< -100 millivolts) over depth intervals of tens of meters (U.S. Department of Energy, 1999). In contrast, pH remains relatively constant over the entire interval measured. Evidence for variations in water chemistry over time (tens of years) is also present in the data reported by Perfect, et al. (1995) and Oliver and Root (1997), although it is difficult to determine how much of this variability is due to system heterogeneity and how much represents inconsistency in sampling methodology.

B.1.2.2 Stable Isotope Chemistry (δD, $\delta^{18}O$, and $\delta^{13}C$)

With respect to deuterium and ^{18}O, the most depleted samples in the area come from wells in tuffaceous aquifers in Pahute Mesa ($\delta D = -109$ to -114‰ SMOW and $\delta^{18}O = -14.05$ to -14.75‰ SMOW) (White and Chuma, 1987). This is due to the high elevation on Pahute Mesa, and are similar to values sampled from springs and wells in the headwaters of Oasis Valley. A downgradient enrichment in both deuterium and ^{18}O in the Oasis Valley basin is attributed to partial evaporation and progressive mixing between waters originating in Pahute Mesa and heavier waters recharging locally at lower elevations in the Bullfrog Hills ($\delta D = -102$‰ and $\delta^{18}O = -13.30$ to -13.42‰ SMOW). In general, the isotopic signatures for waters from Tertiary volcanic and Quaternary alluvium aquifers overlap. All of the waters fall on a line that parallels the global meteoric water line (GMWL) of Craig (1961), but is shifted to slightly more depleted (~5‰) deuterium values. Assuming that the effects due to changes in elevation (i.e., erosion) are negligible, several authors infer that this shift is due to a cooler climate during the period of recharge (White and Chuma, 1987; Stuckless, et al., 1991). In contrast, recent regional studies (Davisson, et al., 1999) have suggested that there is a systematic increase in $\delta^{18}O$ from north to south. These trends, corrected for the effects of evaporation, reveal narrow plumes of ^{18}O-depleted water extending to the south between mountain ranges. Davisson, et al. (1999) have used these data trends to suggest that recharge of groundwater occurs to the north at higher elevations, with regional groundwater flow along north-south trending Basin and Range valleys. Further constraining these data with ^{14}C groundwater ages also suggests short travel times on the order of < 10,000 years, arguing against climate change as the cause of stable isotope depletion.

The waters collected from volcanic aquifers beneath Yucca Mountain are significantly heavier ($\delta D = -100$ to -108‰ and $\delta^{18}O = -13.4$ to -14.2‰ SMOW) than waters collected at Pahute Mesa. They are still shifted to a line parallel to the GMWL, but the shift is slightly less than that observed by White and Chuma (1987) for Pahute Mesa and Oasis Valley. Stuckless, et al. (1991) use this evidence to indicate that there is little communication between recharge at Pahute Mesa and the waters beneath Yucca Mountain. At least in part, this lack of communication may be an explanation for the discrepancy between calculated ($\delta D = -110$‰ SMOW) and measured ($\delta D = -114$‰SMOW) values for Pahute Mesa in the deuterium calibrated mixing model of Feeney, et al. (1987).

Additional evidence related to mixing is in the isotopic character of groundwater samples from Fortymile Canyon. These samples are enriched in both deuterium and ^{18}O relative to all other water samples from the Yucca Mountain region ($\delta D = -92.0$ to -97.5‰ and $\delta^{18}O = -12.4$ to

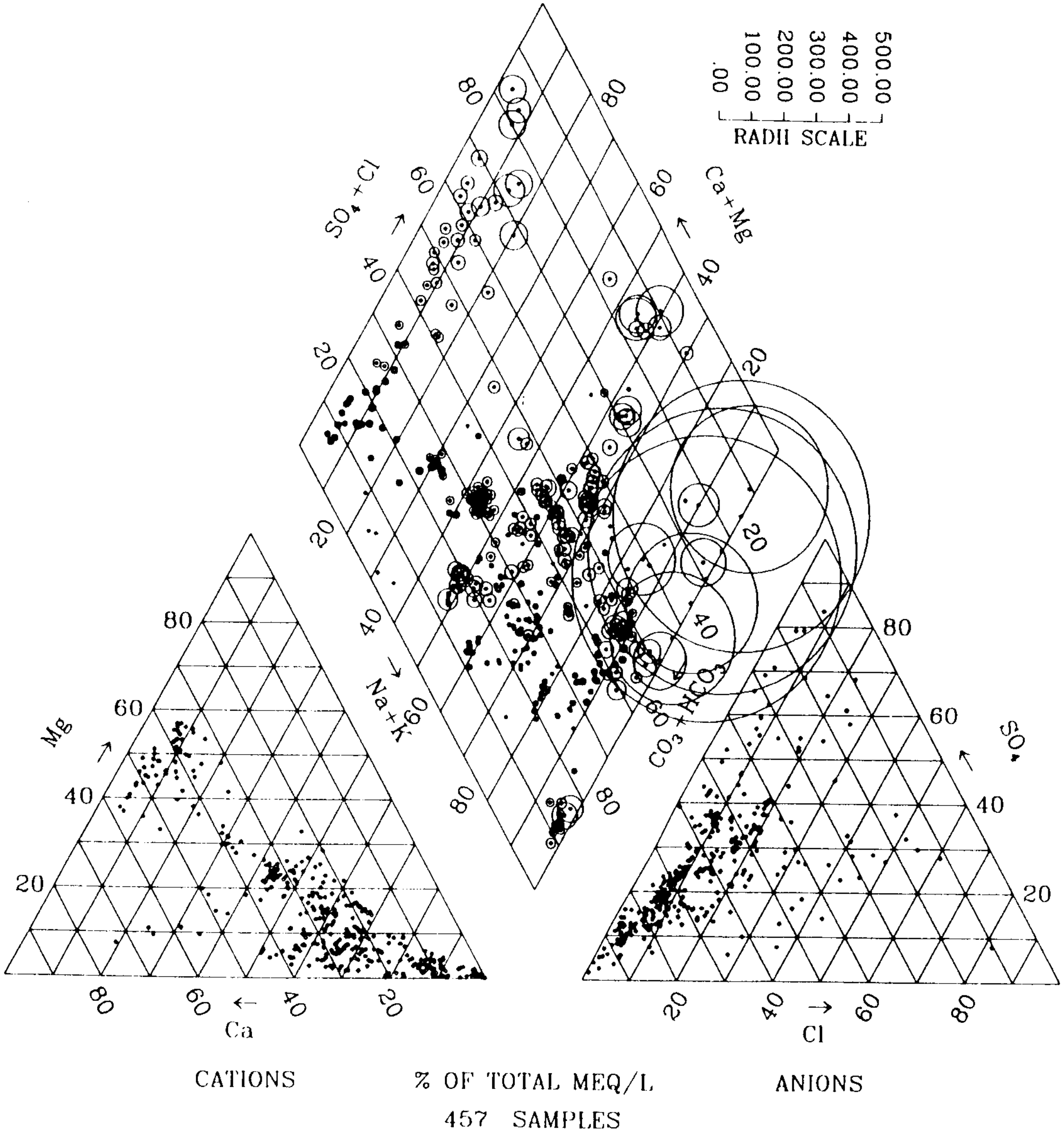

Figure B-2. Saturated zone water chemistry in meq/L. Circle diameter represents total dissolved solid concentration (from Perfect, et al., 1995)

−13.0‰ SMOW). From this evidence, it seems that there is little communication between the Tertiary aquifers beneath Fortymile Canyon and those to the west under Yucca Mountain (White and Chuma, 1987; Stuckless, et al., 1991). Groundwater from the upper reaches of Fortymile Canyon is closer to the modern GMWL, suggesting local, relatively recent recharge, predominantly from summer precipitation at lower elevations. Claassen (1985) used this information to support inferred overland flow and recharge in Fortymile Canyon out into drainages in the Amargosa Desert. In this model, the chemical composition of the groundwater is principally determined by interaction with alluvial fill, with little input from tuff aquifers upgradient. This would tend to argue against significant mixing and dilution between tuff groundwaters beneath Yucca Mountain, and those in the alluvial aquifers in Fortymile Canyon. An alternative proposal (White, 1981; White and Chuma, 1987) suggests that groundwater in the Amargosa Desert originated from tuffs in Fortymile Canyon with little interaction with alluvium. In this conceptual model, the Yucca Mountain groundwater is a small fraction of the water balance and mixing is actually quite thorough. There is a gradual depletion in both deuterium and ^{18}O from wells UE-29a#1 and UE-29a#2 in the headwaters of Fortymile Canyon to wells J-12 and J-13 15 km to the south. This trend is the opposite from the enrichment that one might expect either due to progressive water-rock interaction or to evaporation. The isotopic signatures of wells J-12 and J-13 might, instead, be due to mixing between waters flowing from beneath Yucca Mountain downgradient to the southeast (Fridrich, et al., 1994).

Carbon isotope interpretation is complicated by the ready reaction of carbon among different phases in a groundwater/rock/gas system. Some inferences can be drawn from the available data. In Oasis Valley, White and Chuma (1987) observed a general downgradient decrease in δ^{13}C. In the headwater region, relatively enriched ^{13}C values suggest a source derived from mixing between detritus from Paleozoic carbonate outcrops ($\delta^{13}C = +1.4$‰ PDB) to the west and atmospheric CO_2 ($\delta^{13}C \sim -7$‰ PDB). Coupled with an order of magnitude increase in the equilibrium PCO_2 suggests a progressive downgradient reaction of the shallow groundwater system with atmospheric CO_2. Values in the lower reaches are even more depleted, suggesting an increasing input from phreatophytes.

In Fortymile Canyon, measured groundwater δ^{13}C tends to increase from north ($\delta^{13}C = -13.1$‰ PDB in UE-29a#2) to values of about −7 to −8‰ PDB in the southern reaches of Fortymile Canyon and northern Amargosa Desert (White and Chuma, 1987). Samples in the central Amargosa Desert about 10 to 15 km south of the town of Amargosa Valley are enriched still further (Claassen, 1985) to $\delta^{13}C = -3.4$ to -4.4‰ PDB. Heavier $\delta^{13}C = -5.7$ to -6.2‰ PDB are also reported (Claassen, 1985) in the south central Amargosa Desert near the Nevada-California state line at the base of the Funeral Mountains, and just south of U.S. Highway 95 about 5 km south of Bare Mountain. Claassen (1985) used these carbon isotope results to support overland recharge through Fortymile Canyon into drainages in northern and eastern Amargosa Desert. More negative values to the north are due to plant respiration ($\delta^{13}C \sim -24$ to -25‰ PDB) exerting a larger control on carbon isotope systematics at higher elevations and shallower depths to water in wells UE-29a#1 and UE-29a#2. With progressive flow to the south, δ^{13}C increases through increasing interaction with atmospheric CO_2 and fractured calcite. In the southern areas, the highest δ^{13}C values may be due either to progressive mixing with groundwaters from the carbonate aquifers (Claassen, 1985; Stuckless, et al., 1991; Fridrich, et al., 1994) or perhaps to increased interaction with carbonate alluvium that originated in the Paleozoic carbonate uplands in the Spring, Funeral, and Bare Mountains (White and Chuma, 1987).

B.1.2.3 Radiogenic Isotopes

Age-dating using ^{14}C also supports the general flow from north to south in Fortymile Canyon, with the youngest (uncorrected ^{14}C) measured in UE-29a#1 and UE-29a#2, and increasing in age to the south in wells J-12 and J-13. As is the case with deuterium and ^{18}O data, waters from Fortymile Canyon are distinctly "younger" (higher ^{14}C) than those in the tuff aquifers beneath Yucca Mountain, supporting the hypothesis of limited mixing between these two groundwaters. It is still possible that mixing between recharge waters in Fortymile Canyon with older groundwaters from beneath Yucca Mountain produces the observed ages in J-13 and J-12, although the complexities of carbon systematics complicate the interpretation.

Peterman and Stuckless (1993) reported the results of strontium analyses for groundwaters in the vicinity of Yucca Mountain. In general, there is an increase in $\delta^{87}Sr$ from the Spring Mountains ($\delta^{87}Sr = -0.5‰$) toward the west and the springs at Ash Meadows ($\delta^{87}Sr = 6$ to 13.1‰), suggesting increased interaction with Cambrian and Precambrian clastics. There is also a general downgradient increase in $\delta^{87}Sr$ from Pahute Mesa to Franklin Lake Playa. Peterman and Stuckless (1993) suggest that this trend represents progressive water rock interaction within the volcanic units south to Amargosa Valley, where interaction with alluvial fill and increased mixing from groundwaters below the valley fill result in a general increase. The highest values to the south may be a result from upwelling, or possibly interaction with alluvial fill made up of Precambrian debris from the Funeral Mountains. Peterman and Stuckless (1993) also observed about 3 per mil "noise" in the $\delta^{87}Sr$ data obtained from wells in volcanic tuffs north of the Amargosa Desert. This probably reflects the 10 per mil range in $\delta^{87}Sr$ for the different volcanic units and the complex structure that results in different lithologic units at the water table and complex flow. The fact that these heterogeneities are to some extent preserved in the "noise" suggests that mixing of fluids may be limited beneath Yucca Mountain.

B.1.3 PERCHED WATER

A number of perched zones have been found at Yucca Mountain (Burger and Scofield, 1994: Yang, et al., 1996a, 1998; Bodvarsson and Bandurraga, 1997; Wu, et al., 1997). Perched zones have been found on the basal vitrophyre of the Topopah Spring Tuff and within the Calico Hills Formation. As of June 1996, all perched water found occurs below the repository horizon. Boreholes USW UZ#1 and USW UZ#14, which are on the same drilling pad, encountered a perched zone. The perched water is 190 m above the water table, and the zone was extensive enough to be pump tested at a rate of 0.9 gpm (0.06 L/s) for 67 hr, and a total of 6,000 gal. (22,700 L) were produced. It has been estimated that this perched water zone is much more extensive than originally thought, with an approximate volume of 30 million gal. (113,560,000 L). Perched water was also found in USW SD-9, which appeared to be coming from just above the basal vitrophyre of the Topopah Spring. This perched water is 120 m above the water table. Perched water has also been detected within the Calico Hills Tuffs. Boreholes that encountered perched water within the Calico Hills Tuffs include USW SD-7 and USW NRG 7/7a. The perched zone encountered by SD-7 was extensive enough to be pump tested at a rate of 3.3 gpm (0.21 L/s) for 30 hr and a total of 12,000 gal. (45,400 L) was produced.

Water chemistry data for the perched zones are reported in Yang, et al. (1996a,b) and summarized in Figure B-3. Current information includes major and minor elements, stable isotopes (δD, $\delta^{18}O$, $\delta^{13}C$), and radiogenic isotopes (^{14}C, $^{87}Sr/^{86}Sr$). These data indicate that perched water major element chemistry is distinct from matrix water chemistry in the unsaturated zone (Yang, et al., 1996a) and more similar to the water chemistry from the saturated zone (e.g., McKinley, et al., 1991; Perfect, et al., 1995). In general, the perched water is more dilute than the unsaturated zone pore waters, with lower chloride concentrations (about 4 to 8 mg/L, with one sample up to 15 mg/L). The lower chloride concentration suggests that the perched water forms with less interaction with the host rock, suggesting a fracture source. The differences in water chemistry also indicate that the perched water is not in equilibrium with the pore water. Detectable bomb pulse tritium indicates that there is at least some rapid recharge of the perched water zones, and radiogenic ^{14}C indicates a young residence time relative to groundwater and porewater apparent ^{14}C ages of about 7,000 yr (Yang, et al., 1996a). Deuterium and ^{18}O stable isotope chemistry indicates that perched water is isotopically heavier than saturated zone water and close to the current Yucca Mountain local meteoric water line. The heavier ^{18}O values suggest that the perched water does not contain a significant portion of isotopically light water from the last ice age (10,000 yr) supporting an age of <10,000 yr, although this is not exclusive of older water with a similar isotopic signature. The similarity to the Yucca Mountain local meteoric water line suggests that recharge of the perched water bodies is through local precipitation, principally during winter storm events, rather than from higher elevations to the north.

B.1.4 GAS CHEMISTRY

Analyses of gases collected from the vadose zone at Yucca Mountain at depths up to 140 m show them to be indistinguishable from atmospheric air with regard to major components (78 percent N_2, 21 percent O_2, and approximately 1 percent Ar). However, the CO_2 content is elevated typically at 0.1 to 0.13 percent, and CH_4 is depleted with little to none present, relative to atmospheric values (Thorstenson, et al., 1990). For reference, the CO_2 content of air is approximately 0.03 percent. The CO_2 contents of gases calculated to be at equilibrium with saturated zone well waters from tuffaceous aquifers generally range from 0.13 to 1.4 percent (Kerrisk, 1987). Hence, the maximum CO_2 content of the unsaturated zone gas phase corresponds approximately to the minimum CO_2 content calculated for gases in equilibrium with saturated zone waters. This observation suggests that degassing of saturated zone water could provide CO_2 to the unsaturated zone. The relatively light carbon isotopic character of the gas at Yucca Mountain (e.g., $\delta^{13}C$ normally between −15 and −23‰ PDB) (Thorstenson, et al., 1990; Yang, et al., 1993) indicates a biogenic origin for the carbon. Ground gas that escapes from borehole USW UZ#6S and gas collected from shallow neutron holes on Yucca Mountain have ^{14}C contents generally in excess of 100-pmc indicating that the carbon system has a component derived from testing of nuclear devices (Thorstenson, et al., 1990). However, gas collected from depths up to 350 m in borehole USW UZ#1 have progressively lower ^{14}C activities with depth (Yang, et al., 1993) suggesting that the carbon has been isolated from the atmosphere for longer times with increasing depth.

Because of the generally large liquid saturation in the natural vadose zone, the natural vadose ground gas would be expected to be close to chemical saturation with water at ambient temperatures.

Triay, et al. (1997) provides a detailed summary of the laboratory and modeling studies performed by the LANL on mechanisms that affect radionuclide transport from the proposed

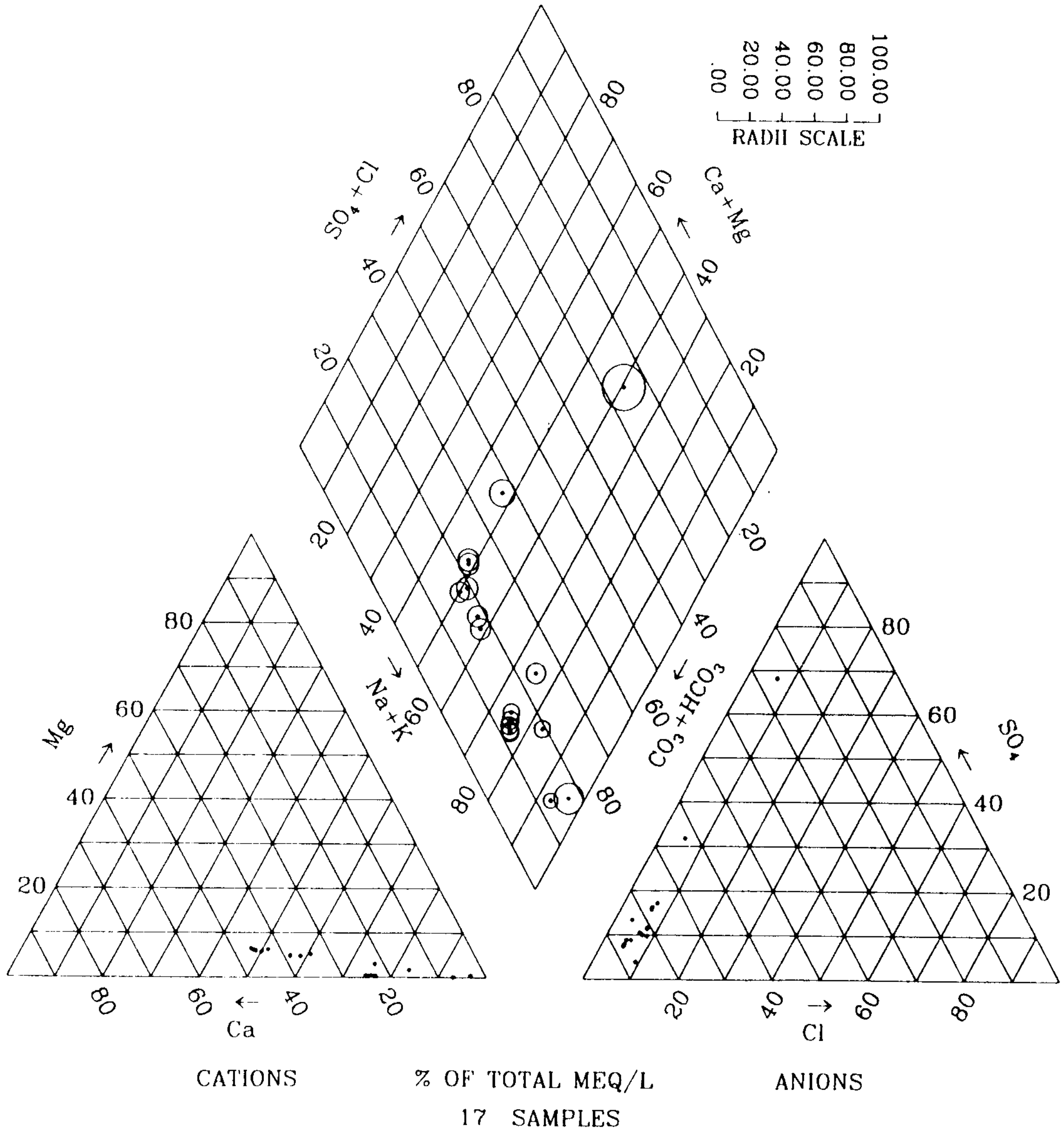

Figure B-3. Perched water chemistry in meq/L. Circle diameter represents total dissolved solid concentration (from Yang, et al., 1996a).

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repository such as sorption, desorption, precipitation, dissolution, and diffusion. The transported radionuclides occur as dissolved species and as particulates and colloids or sorbed to nonradioactive particulates and colloids.

Batch sorption experiments were performed to determine K_d as a function of mineralogy, groundwater chemistry, sorbing element concentration, atmospheric conditions, and temperature. The range of conditions of the experiments were to represent those found in the farfield at Yucca Mountain, where chemical and physical changes are not expected, due to the emplacement of the hot radioactive waste. As described by Meijer (1990), the valid use of the constant K_d approach to describe radionuclide transport requires constant chemistry of the groundwater. Constant chemistry conditions are most likely to be found in the farfield.

All the batch sorption experiments were performed at room temperature. They involved first pretreating the crushed solid phase with the water studied that was either J-13 or UE-25p#1 or a synthetic groundwater of similar composition. The intent of the pretreatment was to minimize the possibility that highly sorptive fresh surfaces of the crushed material would result in unnaturally high K_ds. After pretreatment, the solid was separated from the groundwater and 1 g of solid was contacted with 20 mL of radionuclide-bearing groundwater. After the sorption experiment, the phases were separated and radionuclide concentration in the liquid was determined before and after the experiment. The difference was due to sorption on the solid. (Blanks were used to account for sorption on container).

The radionuclides tested using site-specific materials include americium, plutonium, uranium, selenium, technetium, neptunium, strontium, cesium, barium, radium, cerium, europium, protactinium, thorium, tin, and nickel. Lead, zirconium, niobium, actinium, and samarium have not been tested using Yucca Mountain materials. Likewise, carbon, chlorine, and iodine have not been tested, but in TSPA-VA, they are assumed to have a $K_d = 0$ (U.S. Department of Energy, 1998c).

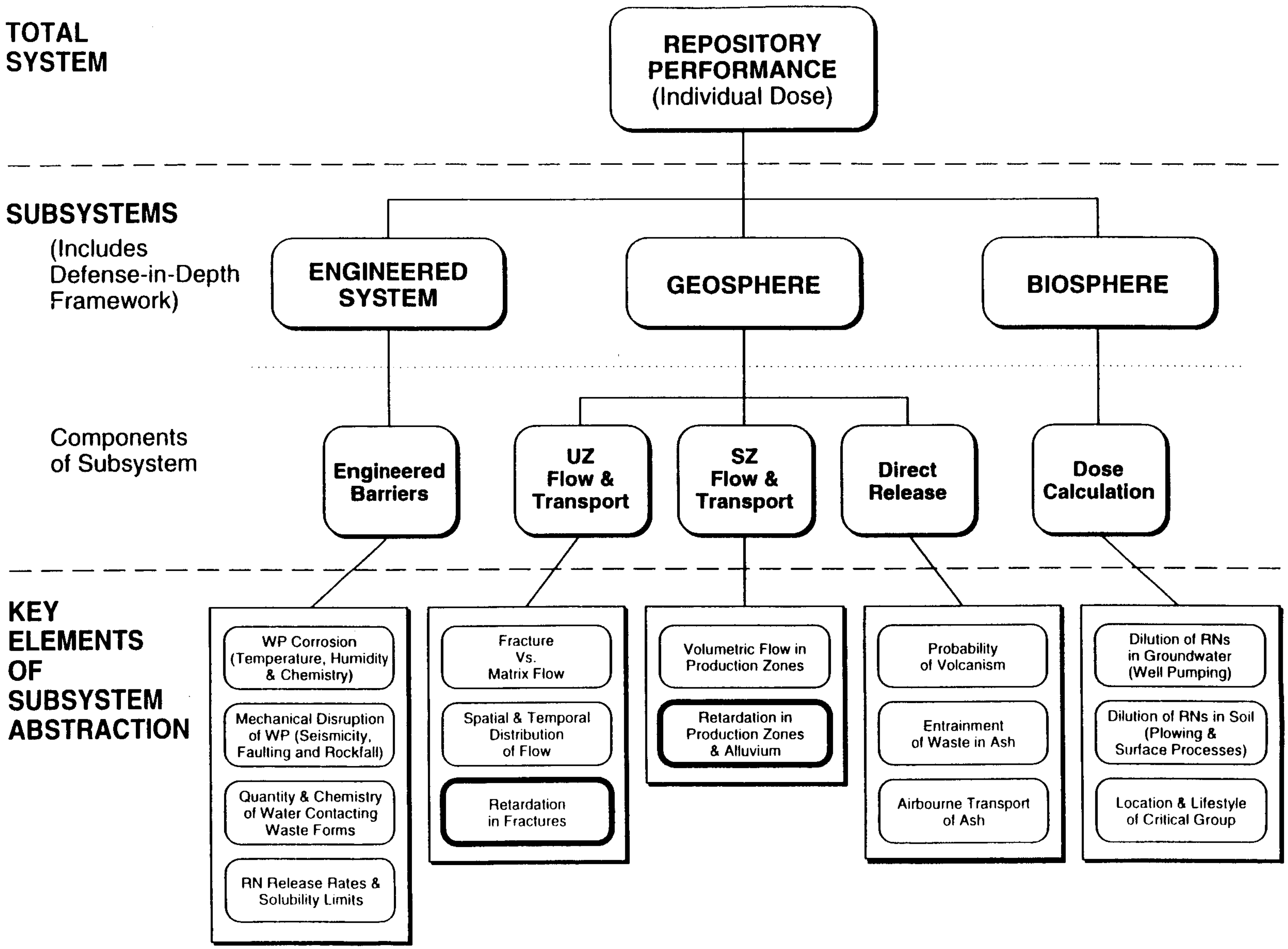

Figure C-1. Flow diagram for Total System Performance Assessment