

**APPENDIX J**  
**DETERMINATION OF WHETHER KINETIC EFFECTS SHOULD**  
**BE INCLUDED IN THE TRANSPORT MODEL**  
**(RESPONSE TO RT 1.04)**

### **Note Regarding the Status of Supporting Technical Information**

This document was prepared using the most current information available at the time of its development. This Technical Basis Document and its appendices providing Key Technical Issue Agreement responses that were prepared using preliminary or draft information reflect the status of the Yucca Mountain Project's scientific and design bases at the time of submittal. In some cases this involved the use of draft Analysis and Model Reports (AMRs) and other draft references whose contents may change with time. Information that evolves through subsequent revisions of the AMRs and other references will be reflected in the License Application (LA) as the approved analyses of record at the time of LA submittal. Consequently, the Project will not routinely update either this Technical Basis Document or its Key Technical Issue Agreement appendices to reflect changes in the supporting references prior to submittal of the LA.

## APPENDIX J

### DETERMINATION OF WHETHER KINETIC EFFECTS SHOULD BE INCLUDED IN THE TRANSPORT MODEL (RESPONSE TO RT 1.04)

This appendix provides a response for Key Technical Issue (KTI) Radionuclide Transport (RT) 1.04, which relates to providing more information about sensitivity studies on  $K_d$ 's for plutonium, uranium, and protactinium, and to evaluate the adequacy of the  $K_d$  data.

#### J.1 KEY TECHNICAL ISSUE AGREEMENT

##### J.1.1 RT 1.04

KTI agreement RT 1.04 was reached during the U.S. Nuclear Regulatory Commission (NRC)/U.S. Department of Energy (DOE) technical exchange and management meeting on radionuclide transport held December 5 through 7, 2000, in Berkeley, California. Radionuclide transport KTI Subissues 1, 2, and 3 were discussed at that meeting (Reamer and Williams 2000).

During the meeting, experiments for plutonium were discussed that showed kinetic effects that make the high flow rates used for the column tests nonrepresentative. Additional sensitivity studies and a review of available data were suggested to evaluate the adequacy of the data. To evaluate the adequacy of the data, the DOE indicated that the effect of plutonium sorption on performance could be investigated in sensitivity studies. As a result of these discussions, KTI agreement RT 1.04 was reached.

The wording of the agreement is:

##### RT 1.04

Provide sensitivity studies on  $K_d$  for plutonium, uranium, and protactinium to evaluate the adequacy of the data. DOE will analyze column test data to determine whether, under the flow rates pertinent to the Yucca Mountain flow system, plutonium sorption kinetics are important to performance. If they are found to be important, DOE will also perform sensitivity analyses for uranium, protactinium, and plutonium to evaluate the adequacy of  $K_d$  data. The results of this work will be documented in an update to the Analysis and Model Report Unsaturated Zone and Saturated Zone Transport Properties available to the NRC in FY 2002.

##### J.1.2 Related Key Technical Issue Agreements

The response to KTI agreement RT 2.05, which was delivered to the NRC in fiscal year 2002, provided a work plan describing the laboratory radionuclide column testing for colloid facilitated transport to be performed for Yucca Mountain project.

The response to KTI agreement RT 1.04 will also satisfy the RT 3.10 agreement, which addresses the unsaturated zone aspect of the same question. KTI agreement RT 3.10 will be

addressed in the context of the unsaturated zone processes in Group Code X, Unsaturated Zone Transport.

## **J.2 RELEVANCE TO REPOSITORY PERFORMANCE**

Radionuclide retardation in the alluvium is expected to delay the movement of most radionuclides for long time periods, varying from thousands to tens of thousands of years for nuclides that tend to sorb onto porous materials. Key sorbing radionuclides include  $^{237}\text{Np}$ ,  $^{241}\text{Am}$ , and  $^{240}\text{Pu}$ . If only solute transport of these three radionuclides is considered, repository performance in the 100,000-year time frame will be most sensitive to  $^{237}\text{Np}$  retardation in the alluvium because  $^{237}\text{Np}$  has a smaller retardation factor than the other radionuclides. However,  $^{240}\text{Pu}$  and  $^{241}\text{Am}$  will be more likely to be transported large distances by colloid-facilitated transport than  $^{237}\text{Np}$ .

Experiments on plutonium show kinetic effects that make the high flow rates used in the column tests nonrepresentative. Additional sensitivity studies and a data review will be used to evaluate the adequacy of the data. The criterion to confirm the  $K_d$  for plutonium determined in the static tests (that are appropriate for calculating retardation in dynamic systems) was evaluated for the adequacy of the data. The effect of plutonium sorption on repository performance has been investigated in sensitivity studies, and external information on plutonium sorption has been reviewed.

A general discussion of the influence of sorption coefficients on radionuclide transport in the saturated zone is found in Section 3.3.2.

## **J.3 RESPONSE**

Sorption kinetics of plutonium have been evaluated to determine if kinetic effects can be neglected in the transport models. If kinetic effects can be neglected, retardation factors, which are based on the validity of the local equilibrium assumption, can be used in the transport equations that simulate the transport of plutonium. The study presented in this response demonstrates that sorption kinetics are relatively unimportant for plutonium and that the assumption of local equilibrium can be used when evaluating transport of plutonium in the saturated zone. Under the conditions in which the Yucca Mountain sorption experiments were performed, the kinetics of plutonium sorption were slower than those of other sorbing radionuclides. Therefore, for typical Yucca Mountain geochemical conditions, kinetic limitations of the sorption reaction do not need to be considered when predicting the transport of radionuclides through the saturated zone.

The information in this report is responsive to agreement RT 1.04 made between the DOE and NRC. The report contains the information that DOE considers necessary for the NRC to review for closure of this agreement.

## **J.4 BASIS FOR THE RESPONSE**

To assess whether sorption kinetic processes need to be included in the transport model, column test data collected under flow rates pertinent to the Yucca Mountain flow system were used to calculate Damköhler ( $Da$ ) numbers (Triay et al. 1997).  $Da$  is a dimensionless number used for

comparing transport and reaction timescales to determine if kinetic limitations apply to a particular reactive transport system. Therefore,  $Da$  can be used to determine if local equilibrium assumptions are valid, and if so, kinetic effects can be neglected and computationally efficient equilibrium models with retardation factors as input can be used.

Plutonium kinetics were examined (BSC 2003, Attachment IV) because plutonium sorption kinetics are slower than the sorption kinetics of other radionuclides in the Yucca Mountain inventory examined in *Site-Scale Saturated Zone Transport* (BSC 2003, Attachment I). Plutonium kinetics may not always be slower than that of other radionuclides. However, for the representative Yucca Mountain geochemical conditions examined (BSC 2003, Attachment IV), plutonium sorption kinetics were slower than that of the other sorbing radionuclides, indicating that plutonium should be chosen for study in this analysis. Thus, if the assumption of local equilibrium is valid for plutonium in these relatively short time-scale experiments (on the order of days), it should be valid for other radionuclides in the Yucca Mountain inventory at relatively long saturated-zone travel timescales (on the order of years). By using plutonium in short timescale experiments, this analysis provides a stringent test for assessing the validity of the local equilibrium assumption.

$Da$  is defined as the first-order rate constant,  $k$  (1/time), multiplied by a representative residence time,  $T$

$$Da = k \times T \quad (\text{Eq. J-1})$$

The rate constant quantifies the reaction timescale of the system, and the residence time quantifies the transport timescale.  $Da$  provides a basis for evaluating which timescale dominates the system. If the reaction time is much faster than the transport time,  $Da$  is large, and the assumption of local equilibrium is valid.

For evaluating sorption behavior, separate  $Da$  numbers,  $Da_{\text{att}}$  and  $Da_{\text{det}}$ , can be computed for attachment and detachment of the sorbing contaminant using  $k_{\text{att}}$  and  $k_{\text{det}}$ , which, respectively, are the attachment and detachment rate constants for plutonium sorbing onto mineral surfaces. Bahr and Rubin (1987, p. 450) found that equilibrium is well approximated when the sum of the two  $Da$  numbers is greater than 100, and it is reasonably well estimated when the sum is greater than 10. Thus, the larger the sum of the two  $Da$  numbers, the more appropriate is the assumption of equilibrium.

Valocchi (1985, Figure 2) found similar results, although only the reverse rate  $k_{\text{det}}$  was used to compute the  $Da$  number. The Valocchi approach is used here because a single, first-order rate produced the best fit to the column experiments. Because the Valocchi approach uses only one  $Da$  number and gives a lower  $Da$  number than the Bahr and Rubin method, the Bahr and Rubin (1987, p. 450) criteria of 10 and 100 can conservatively be used with the Valocchi approach.

To estimate the  $Da$  number for the saturated zone transport model (Equation J-1), the reaction rate constants for plutonium sorption must be determined. This is done with laboratory data from column experiments (BSC 2003, Attachment IV). The general idea behind the calculation is to fit a first order reaction rate constant to  $^{239}\text{Pu}$  column data. This rate constant, along with a

conservative travel time through the fractured volcanics, can be used to estimate a  $Da$  number. The  $Da$  number was determined to be greater than 100, indicating that kinetic limitations are not important for plutonium in the saturated zone at Yucca Mountain (BSC 2003, Attachment IV). Under the conditions in which the Yucca Mountain sorption experiments were performed, the kinetics of plutonium sorption were slower than those of other sorbing radionuclides (BSC 2003, Attachment IV). Therefore, for typical Yucca Mountain geochemical conditions, kinetic limitations of the sorption reaction do not need to be considered when predicting the transport of radionuclides through the saturated zone.

Colloid facilitated transport cannot be ruled out in the column experiments of Triay et al. (1997) used in this analysis. The kinetic interpretation of these column studies is consistent with a colloid transport interpretation where the sorption and desorption rate constants are equivalent to colloid filtration and detachment rate constants. However, if the early plutonium breakthroughs in the column experiments were a result of colloid-facilitated transport of a portion of the plutonium, then the sorption of rate constants for the soluble plutonium fraction would have to be greater than those deduced assuming that all the plutonium was soluble. This scenario would only strengthen the conclusion that the equilibrium approximation is valid for soluble plutonium over large timescales.

In summary, the kinetics of plutonium sorption were slower than those of other sorbing radionuclides. Therefore, for typical Yucca Mountain geochemical conditions, kinetic limitations of the sorption reaction do not need to be considered when predicting the transport of radionuclides through the saturated zone.

## J.5 REFERENCES

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**APPENDIX K**  
**TRANSPORT— $K_{ds}$  IN ALLUVIUM**  
**(RESPONSE TO RT 2.06, RT 2.07, AND GEN 1.01 COMMENTS 41 AND 102))**

### **Note Regarding the Status of Supporting Technical Information**

This document was prepared using the most current information available at the time of its development. This Technical Basis Document and its appendices providing Key Technical Issue Agreement responses that were prepared using preliminary or draft information reflect the status of the Yucca Mountain Project's scientific and design bases at the time of submittal. In some cases this involved the use of draft Analysis and Model Reports (AMRs) and other draft references whose contents may change with time. Information that evolves through subsequent revisions of the AMRs and other references will be reflected in the License Application (LA) as the approved analyses of record at the time of LA submittal. Consequently, the Project will not routinely update either this Technical Basis Document or its Key Technical Issue Agreement appendices to reflect changes in the supporting references prior to submittal of the LA.

## APPENDIX K

### TRANSPORT— $K_d$ s IN ALLUVIUM (RESPONSE TO RT 2.06, RT 2.07, AND GEN 1.01 (COMMENTS 41 AND 102))

This appendix provides a response for Key Technical Issue (KTI) agreements Radionuclide Transport (RT) 2.06, RT 2.07 and General Agreement (GEN) 1.01 Comments 41 and 102. These KTI agreements relate to providing more information about how the U.S. Department of Energy (DOE) used testing in the alluvium to develop  $K_d$ s for use in the model.

#### K.1 KEY TECHNICAL ISSUE AGREEMENTS

##### K.1.1 RT 2.06, RT 2.07, and GEN 1.01 (Comments 41 and 102)

KTI agreements RT 2.06 and RT 2.07 were reached during the U.S. Nuclear Regulatory Commission (NRC)/DOE technical exchange and management meeting on radionuclide transport held December 5 through 7, 2000, in Berkeley, California. Radionuclide transport KTI Subissues 1, 2, and 3 were discussed at that meeting (Reamer and Williams 2000).

At this technical exchange, the NRC suggested that, for the valid application of the constant  $K_d$ s approach, the DOE should demonstrate that the flow path acts as a single continuum porous medium. The DOE stated that evidence that the alluvium can be modeled as a single continuum porous medium would be obtained by testing at the Alluvium Testing Complex.

The NRC further suggested that, for the valid application of the constant  $K_d$ s approach, the DOE should demonstrate that appropriate sorption values have been adequately considered (e.g., experimentally determined or measured). The DOE responded that preliminary transport parameter values derived from lab measurements in performance assessment analyses would be used. The DOE would refine and confirm these parameter values after multiple borehole tracer testing of radionuclide surrogates at the Alluvium Testing Complex and after laboratory batch and column radionuclide transport studies.

During the NRC/DOE technical exchange and management meeting on thermal operating temperatures, held September 18 through 19, 2001, the NRC provided additional comments relating to these RT KTI agreements (Reamer and Gil 2001). Comments relating to transport  $K_d$ s in alluvium resulted in KTI agreement GEN 1.01, Comments 41 and 102. The DOE provided initial responses to these comments (Reamer and Gil 2001).

Wording of the agreements is:

##### RT 2.06

If credit is taken for retardation in alluvium, the DOE should conduct  $K_d$  testing for radionuclides important to performance using alluvium samples and water compositions that are representative of the full range of lithologies and water chemistries present within the expected flow paths (or consider alternatives such as testing with less disturbed samples, use of samples from more accessible analog sites (e.g., 40-mile Wash), detailed process level modeling, or other

means). DOE will conduct  $K_d$  experiments on alluvium using samples from the suite of samples obtained from the existing drilling program; or, DOE will consider supplementing the samples available for testing from the alternatives presented by the NRC. This information will be documented in an update to the SZ In Situ Testing AMR, available in FY 2003.  $K_d$  parameter distributions for TSPA will consider the uncertainties that arise from the experimental methods and measurements.

#### **RT 2.07**

Provide the testing results for the alluvial and laboratory testing. DOE will provide testing results for the alluvial field and laboratory testing in an update to the SZ In Situ Testing AMR available in FY 2003.

#### **GEN 1.01 (Comment 41)**

The new  $N_p$  sorption coefficient distribution for the saturated zone used in the uncertainty analysis needs further analysis. Any future adoption of this distribution in TSPA will require a technical basis consistent with agreements RT 1.05 and RT 2.10.

#### **DOE Initial Response to GEN 1.01 (Comment 41)**

Alluvium  $K_d$  distributions are based on data obtained using EWDP-3S water and alluvium from saturated zone 3S, 9Sx, and 2D. However, DOE acknowledges that 3S water was contaminated with a polymer / surfactant used during well development. The effect of this polymer / surfactant on  $K_d$  values is being investigated by conducting additional experiments using alluvium samples and water from Nye County EWDP well locations along Fortymile wash, which were drilled without using polymer or surfactant additives. These locations are essentially along the projected SZ flow pathway from the proposed repository. The technical basis for sorption coefficients will be provided consistent with the cited agreements for data used in any potential license application.

#### **GEN 1.01 (Comment 102)**

The DOE states in Section 12 (p. 12-4) that 'new data from column and batch experiments have been used to define the  $K_{ds}$  estimate for neptunium-237.' Previous work used uranium  $K_d$  values to characterize the  $K_d$  values for neptunium-237. Has this been improved by using neptunium studies?

#### **DOE Initial Response to GEN 1.01 (Comment 102)**

$K_d$  values obtained directly from neptunium sorption measurements are superior to assuming that uranium  $K_d$  values also apply to neptunium. A description of column and batch Neptunium 237 experiments and results will be provided in the next revision of the transport properties report, per KTI agreements RT 1.05 and RT 2.10.

### **K.1.2 Related Key Technical Issue Agreements**

None.

## **K.2 RELEVANCE TO REPOSITORY PERFORMANCE**

The subject of these agreements is the assessment of  $K_d$  testing to evaluate the retention capacities of Yucca Mountain alluvium for  $^{129}\text{I}$ ,  $^{99}\text{Tc}$ ,  $^{237}\text{Np}$ , and  $^{233}\text{U}$  as part of the characterization of saturated zone flow and transport. The adequate characterization of saturated zone flow and transport is important to performance assessment. Characterization of  $K_d$ s comprises part of the site characterization activities and a description of radionuclide transport. As direct input to the site-scale saturated zone flow model,  $K_d$ s potentially effect the model output and performance assessment. The assessment of  $K_d$ s supports the characterization of the saturated zone processes and their effectiveness; subsequently, it supports the performance assessment.

A discussion of the influence of sorption coefficients on radionuclide transport in the saturated zone is found in Section 3.3.2.

## **K.3 RESPONSE**

### **K.3.1 Response to RT 2.06, RT 2.07, and GEN 1.01 (Comments 41 and 102)**

The alluvium south of Yucca Mountain is expected to retard the migration of radionuclides from the repository to the accessible environment. The alluvium consists primarily of materials of volcanic origin, with some enrichment of clays and zeolites relative to the volcanic tuffs at Yucca Mountain. Analyses of selected samples by X-ray diffraction indicate the dominant phases in the alluvium are quartz, feldspar, and cristobalite, followed by smectite and clinoptilolite. These results are consistent with a volcanic origin for the alluvium south of Yucca Mountain.

A series of experiments were conducted to better characterize the retardation potential of saturated alluvium. The objectives of the experiments were to:

- Evaluate the retardation potential of alluvium for  $^{129}\text{I}$ ,  $^{99}\text{Tc}$ ,  $^{237}\text{Np}$ , and  $^{233}\text{U}$  by determining distribution coefficients ( $K_d$ ; ml/g) using alluvium samples and water collected from boreholes in saturated alluvium along potential flow paths to the accessible environment
- Study chemical reaction mechanisms between these four radionuclides and alluvium
- Estimate sorption and transport parameters for use in predictive models.

To achieve these objectives, batch sorption, batch desorption, and flow-through column experiments were conducted under ambient conditions (room temperature, contact with atmosphere) to determine  $K_d$  values for the four radionuclides in alluvium samples from different boreholes. The first set of sorption experiments was carried out using alluvium samples from the boreholes drilled in Phase 1 of the Nye County Early Warning Drilling Program (NC-EWDP-1X,

NC-EWDP-2D, NC-EWDP-3S, NC-EWDP-9SX, NC-EWDP-19D). Groundwater from borehole 3S was used in experiments with samples from boreholes 1D, 2D, 3S, and 9SX, while groundwater from borehole 19D was used in experiments with alluvium samples from 19D. Because groundwater from borehole 3S may not be representative of in situ conditions in this borehole (i.e., the water obtained from borehole 3S may have contained materials used in borehole construction), the results obtained in experiments with samples from boreholes 2D, 3S, and 9S were not used in the derivation of sorption coefficient probability distributions used in the total system performance assessment for the license application. The second set of experiments was carried out using alluvium samples from three boreholes (NC-EWDP-10SA, NC-EWDP-19M1A, and NC-EWDP-22SA) and groundwater from different zones in NC-EWDP-19D (Zones 1 and 4) and NC-EWDP-10SA.

As a group, the samples selected for sorption experiments are taken to be representative of alluvium in the flow path to the accessible environment. Boreholes NC-EWDP-10SA, 19D, 19M1A, and 22SA are located within or close to the active channel in Fortymile Wash. The groundwater in these boreholes is, on average, more oxidizing than groundwater measurements from boreholes west (NC-EWDP-1D, 3S, 7S, 9S, 12PA, 12PB, 12PC, 15D, and 15P) or east (NC-EWDP-4P, 5S) of the Fortymile Wash (DTN: LA0206AM831234.002). Oxidizing groundwater should result in smaller  $K_d$  values for neptunium and uranium than reducing groundwater. For neptunium, the change in sorption behavior occurs at approximately  $230 \pm 30$  mV at near-neutral pH (Langmuir 1997, p. 538). For uranium, the change in sorption behavior occurs at lower Eh values in the range 0.0 to 100 mV at near-neutral pH (Langmuir 1997, p. 506). Thus, the derivation of sorption coefficient probability distributions using sorption data obtained on samples from boreholes NC-EWDP-10SA, 19D, and 19M1A leads to conservatism in the prediction of transport rates in alluvium.

Results of the batch tests suggest that the interaction of  $^{129}\text{I}$  and  $^{99}\text{Tc}$  with the alluvium is negligible. Therefore, no additional credit is taken in total system performance assessment for retardation of these radionuclides in alluvium.

Measured  $K_d$  values for  $^{237}\text{Np}$  in alluvium ranged from about 3 to 13 ml/g, excluding experiments with 3S water and experiments with particle sizes less than 75  $\mu\text{m}$ . The less than 75  $\mu\text{m}$  size fraction is enriched in clays and represents a small weight fraction of in situ alluvium. Column experiments with borehole NC-EWDP-19D alluvium and water indicate that the extent of neptunium retardation depends on the flow rate through the columns. A column experiment using a flow rate (43 m/yr) in the range of rates predicted for the alluvial aquifer (10 to 80 m/yr) (BSC 2003) did not show effective neptunium breakthrough even after the elution of about 12.5 pore volumes. This result implies the neptunium sorption coefficient in this column was greater than 2.7 ml/g. The batch  $K_d$  measured for this material was 6.9 ml/g. In column experiments with an effective flow rate of 210 m/yr, a fraction of the neptunium broke through with an effective  $K_d$  value of 1.5 ml/g, and when the flow rate was about 700 m/yr, a fraction broke through with an effective  $K_d$  value of only 0.1 ml/g. However, most of the neptunium was retained on the columns in these experiments. The difference between the batch result and the minimum  $K_d$  values from the column tests cannot be explained entirely by a single first-order kinetic reaction mechanism. The results are more consistent with multiple sorption sites with different sorption rates and  $K_d$  values in the alluvium. Mass transfer processes also may contribute to the observed behavior. However, the result of an effective  $K_d$  value greater

than 2.7 ml/g in the column experiment with a linear flow velocity approximating estimated flow velocities in the alluvium is consistent with the concept that, as flow rates approach in situ conditions, the use of batch neptunium  $K_d$  values is justified in total system performance assessment calculations.

For  $^{233}\text{U}$ ,  $K_d$  values measured in batch experiments ranged from about 1 to 9 ml/g in alluvium. The experimental results indicate that water chemistry has a strong influence on the sorption behavior of uranium in contact with alluvium. When groundwater from Zone 1 in borehole NC-EWDP-19D was used in sorption experiments with alluvium samples from boreholes 19IM1A and NC-EWDP-22SA, sorption coefficient values of 3 to 9 ml/g were obtained. When groundwater from Zone 4 in borehole 19D was used in the sorption experiments with separate aliquots of the same alluvium samples, sorption coefficient values of 1 to 3 ml/g were obtained. The main differences in the chemistry of groundwater from Zones 1 and 4 in borehole 19D include lower  $\text{Ca}^{2+}$  (0.92 versus 3.7 mg/L) and higher pH in Zone 4 (7.7 versus 9.0), and lower dissolved oxygen content in Zone 1 (0.7 mg/L versus 3.3 mg/L). The low dissolved oxygen content of Zone 1 groundwater implies more reducing conditions, and this may explain the differences in uranium sorption behavior in experiments with these two waters. In addition, the higher pH in Zone 4 causes a greater carbonate content in Zone 4, which results in uranium carbonate complex formation, thus decreasing its sorption capacity.

A limited number of uranium column experiments were carried out with alluvium. The experiments were run at an elution rate of 10 ml/hr, which corresponds to a linear flow velocity at least an order of magnitude faster than estimated in in situ alluvium flow velocities. At this elution rate, a small fraction of the uranium breaks through with tritium, indicating that this fraction of uranium was transported through the column with no retardation. However, most of the uranium was not eluted over the duration of the experiments. Long tails on the uranium breakthrough curves, and the incomplete recovery of uranium from the column experiments, suggest that the bulk of the  $^{233}\text{U}$  was slow to desorb even at an elution rate of 10 ml/hr.

When compared to the results obtained from column experiments using neptunium, the retardation of uranium in the columns at flow rates similar to those anticipated in the natural system, is expected to be close to that predicted by the results of batch experiments. However, more column tests at lower flow velocities are required to verify this expectation and ultimately to validate the use of batch uranium  $K_d$  values in alluvium for total system performance assessment calculations. In effect, the results of the uranium column experiments are not appropriate for use in the derivation of the uranium sorption coefficient probability distribution in alluvium because flow rates exceeded in situ rates expected in the alluvium.

There is a range of redox conditions in alluvial groundwaters, as measured in groundwaters pumped from Nye County boreholes. Groundwater along the easternmost (i.e., NC-EWDP-5S) and westernmost (i.e., NC-EWDP-1DX, 3D) potential flow paths to the accessible environment shows reducing characteristics. Groundwater measurements from boreholes along the central portion of the flow system (e.g., NC-EWDP-19D and NC-EWDP-22S) generally shows more oxidizing conditions, although not exclusively, as indicated by the NC-EWDP-19D Zone 1 water. The sorption coefficient probability distribution for uranium in alluvium was formulated to take this variability into account.

The information in this report is responsive to agreements RT 2.06, RT 2.07, and GEN 1.01 (Comments 41 and 102) made between the DOE and NRC. The report contains the information that DOE considers necessary for the NRC to review for closure of these agreements.

#### K.4 BASIS FOR THE RESPONSE

##### K.4.1 Materials Used in Recent Alluvium Batch Sorption and Column Transport Experiments (Used for Developing $K_d$ Distributions)

Alluvium samples were obtained at various depths from three boreholes located south of Yucca Mountain (NC-EWDP-19IM1A, NC-EWDP-10SA, and NC-EWDP-22SA). For the batch experiments, the alluvium samples were dry sieved. For the column experiments, alluvium samples with particle sizes ranging from 75 to 2000  $\mu\text{m}$  were wet sieved to remove fine particles that would clog the columns. Groundwater used in the experiments was obtained from boreholes NC-EWDP-19D (Zones 1 and 4) and NC-EWDP-10SA. The characteristics and chemical composition of NC-EWDP-19D waters is summarized in Table K-1. Field measurements of the redox conditions in groundwater samples in alluvium are shown in Table K-2.

Table K-1. Chemical Composition of Water from Borehole NC-EWDP-19D

Characteristics and Chemical Species	Concentration in Zone 1 (mg/L)	Concentration in Zone 4 (mg/L)
Temperature ( $^{\circ}\text{C}$ )	32	31
pH	7.66	9.02
Eh (mV-SHE)	342.1	493.9
$\text{Na}^+$	91.50	107.30
$\text{K}^+$	3.70	3.40
$\text{Ca}^{2+}$	3.70	0.92
$\text{Mg}^{2+}$	0.31	0.03
$\text{SiO}_2$	22.0	18.7
$\text{F}^-$	2.0	2.7
$\text{Cl}^-$	6.10	5.60
$\text{SO}_4^{2-}$	22.0	18.7
$\text{HCO}_3^-$	189	212

NOTE: pH and Eh were measured in the laboratory under the conditions of the batch sorption and column transport experiments (DTN: LA0302MD831341.004). Major ion concentrations are from U.S. Geological Survey measurements reported in DTN: GS011108312322.006.

Table K-2. Redox Measurements in Groundwater in Nye County Boreholes

NC-EWDP Well No.	Sand-Pack Depth (BGS)	Sampling Date	pH	Dissolved Oxygen (mg/L)	Eh mV-SHE	T (°C)
01SX	152-189	5/17/99	7.1	4.3	327	27.5
		11/8/99	7.0	0.9-3.8	128-272	25.9-26.7
		5/18/00	7.1	3.5-3.9	347-407	27.5-27.9
01SX	204-340	5/17/99	7.2	2.7	249	28.4
		11/8/99	7.0	1.4	172	26.9
		5/18/00	7.1-7.2	1.6-1.9	133-146	28.2-28.8
01D	2180.0-2294.7	5/24/00	6.6	0.02	(-51 to -131)	25.9-26.14
03S	245-275	5/20/99	8.6	1.2	370	32.9
		11/15/99	8.3-8.5	1.7-2.2	366-386	30.3-31.9
03S	295-524.3	5/20/99	8.7	0	154	32.5
	Open Hole	11/15/99	8.5-8.9	0.1-0.4	204-299	27.8-32.0
		5/17/00	8.8-9.1	0.08-0.12	(-29 to 41)	32.4-33.9
04PA	394.7-496	5/16/00	8.5-9.8	3.0-6.3	340-456	23.8-26.3
		10/26/00	7.8-7.9	3.8-4.7	309-339	23.5-24.0
04PB	718-849.5	5/26/00	6.4-8.1	6.4-8.1	244-249	26.6-26.9
		10/26/00	9.7-9.9	2.8-3.6	217-242	21.6-23.2
05SB	366.0-499.4	5/17/00	7.5-7.7	0.04-1.5	(-10 to 37)	24.2-27.0
		10/23/00	7.6	0.01-0.09	(-26 to 49)	22.8-24.0
07S	26-53.2	10/23/00	7.0-7.1	0.7-2.4	144-211	19.7-20.6
		3/28/01	6.9-7.0	2.3-2.4	283-301	21.1-21.2
09SX	85.0-126.1	5/19/99	8.3	1.6	388	28.6
		11/10/99	7.6-8.6	2.1-6.4	317-369	25.8-26.6
09SX	134.8-167.1	5/19/99	7.7	5.2	432	28.1
		11/10/99	7.5-7.7	3.6-6.0	354-452	26.1-27.4
09SX	245.4-295.6	5/18/99	7.7	2.9	430	28.5
		11/9/99	7.7-8.1	1.3-3.3	196-251	27.1-27.4
09SX	325-397	5/18/99	7.7	4.8	232	29.0
		11/9/99	7.6-7.7	3.2-4.9	223-303	27.0-27.9
12PA	317.5-389.5	10/25/00	6.4-6.5	0.3-0.5	122-153	27.2-28.9
12PB	316.2-399.75	5/25/00	6.6-6.9	0.6-3.9	33-167	30.5-30.8
		10/25/00	6.5	0.5-0.8	147-160	27.2-27.6
12PC	160.4-249.6	5/25/00	7.1	4.3-5.2	282-302	27.8-27.9
		10/26/00	7.1	5.2-5.5	209-230	24.2-24.4
15P	192.6-274.5	5/23/00	7.7	4.0-4.7	413-424	32.1-32.7
		10/26/00	7.8	4.2-4.4	374-400	26.6-27.5
19D	Zone 1	10/17/00	8.5-8.7	0.8	358-423	31.0-31.3
	408.5-437.0					
19D	Zone 3	9/13/00	8.4	4.8-5.0	388-463	30.3-30.6
	568.0-691.0					
19D	Zone 4	8/27/00	8.8-8.9	3.2-3.4	291-376	31.5-31.6
	717.0-795.0					

Table K-2. Redox Measurements in Groundwater in Nye County Boreholes (Continued)

NC-EWDP Well No.	Sand-Pack Depth (BGS)	Sampling Date	pH	Dissolved Oxygen (mg/L)	Eh mV-SHE	T (°C)
19D	Zone 5	1/5/02	9.0	2.7-3.1	N/A	31.0-32.6
19P	351.5-474.5	5/23/00	8.6-8.7	6.7-7.0	324-396	28.9-29.5
Airport Well		6/10/99	8.3	9.5	370	28.4
YMP WELLS						
WT-17	1312-1359	7/1/98	6.1-6.7	0.0	(-23 to -65)	27.3-29.7
WT-3	1053-1093	6/22/98	7.1-7.6	3.7-6.5	273-422	31.6-33.0

DTN: LA0206AM831234.002.

NOTE: BGS = below ground surface. All measurements in this table were conducted in the field using water freshly pumped from the wells.

Four radionuclides ( $^{129}\text{I}$ ,  $^{99}\text{Tc}$ ,  $^{233}\text{U}$ , and  $^{237}\text{Np}$ ) were used in the experiments.

Mineral characterization of the alluvium used in the experiments was determined by quantitative X-ray diffraction (Table K-3). The major phases in the Yucca Mountain alluvium samples are silica (i.e., quartz, tridymite, cristobalite), K-feldspar, and plagioclase. The amount of smectite and clinoptilolite, which are two major absorptive mineral phases in alluvium, differs among samples. Among these samples, the sum of the smectite and clinoptilolite in NC-EWDP-22SA is larger than in NC-EWDP-19IM1A or NC-EWDP-10SA.

Table K-3. Quantitative X-ray Diffraction Results of Alluvium used in the Experiments

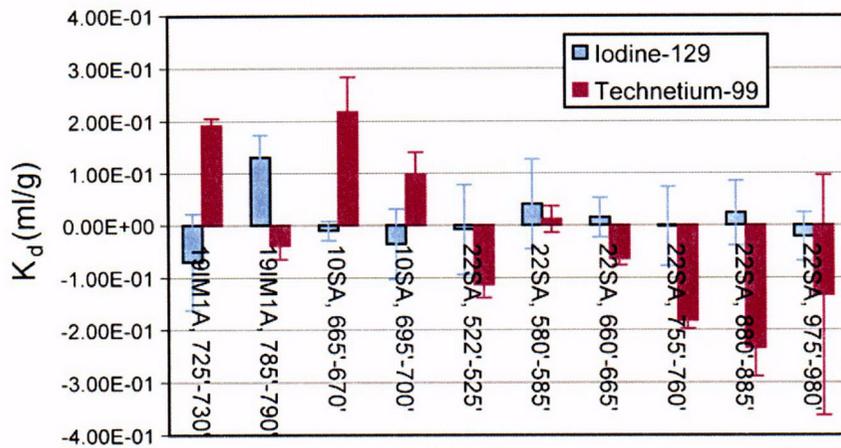
Minerals	Samples (75-500 $\mu\text{m}$ fraction, dry sieve)					
	NC-EWDP-19IM1A		NC-EWDP-10SA		NC-EWDP-22SA	
	725-730 <sup>a, b</sup>	785-790	665-670 <sup>b</sup>	695-700	522-525 <sup>b</sup>	660-665
Smectite	6.9 <sup>b</sup>	6.2	5.7 <sup>b</sup>	2.6	8.3 <sup>b</sup>	4.7
Kaolinite	1.2	1.3	0.8	0.5	2.0	1.1
Clinoptilolite	7.7 <sup>b</sup>	8.5	7.0 <sup>b</sup>	4.1	14.3 <sup>b</sup>	7.9
Tridymite	7.6	7.9	3.5	2.3	8.5	10.2
Cristobalite	5.8	6.4	7.0	5.9	5.6	7.2
Quartz	19.2	16.1	14.0	6.0	12.8	17.3
K-Feldspar	23.7	25.8	29.7	32.5	22.7	25.0
Plagioclase	25.0	26.5	30.5	40.7	19.1	21.2
Biotite	1.0	3.0	3.1	2.5	2.4	2.1
Hematite	0.7	0.7	0.8	2.4	1.0	2.5
Total	98.8	102.3	102.3	99.6	96.7	99.2

Source: Ding 2003, Attachment B.

NOTE: <sup>a</sup> Interval below land surface (feet)<sup>b</sup> Samples selected to conduct kinetic adsorption of  $^{233}\text{U}$ .

### K.4.2 Summary of Batch $K_d$ Values for $^{129}\text{I}$ , $^{99}\text{Tc}$ , $^{233}\text{U}$ , and $^{237}\text{Np}$ in Alluvium

Under ambient conditions, measured  $K_d$  values for alluvium were not statistically distinguishable from zero for  $^{129}\text{I}$  and  $^{99}\text{Tc}$  (Figure K-1).



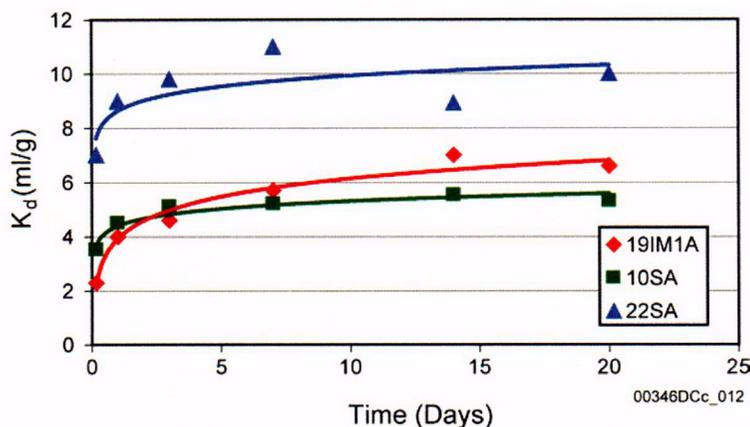
00346DCc\_011

Source: DTNs: LA0302MD831341.001, LA0302MD831341.002.

NOTE: Experiments terminated after two weeks. Liquid to solid ratio was 20 ml/g. NC-EWDP-19D Zone 1 water was used for the experiments with alluvium from NC-EWDP-19IM1A and NC-EWDP-22SA, and NC-EWDP-10S water was used for the experiments with alluvium from NC-EWDP-10SA.

Figure K-1. Batch  $K_d$  Values for  $^{129}\text{I}$  and  $^{99}\text{Tc}$  in Alluvium

$^{237}\text{Np}$  and  $^{233}\text{U}$   $K_d$  values were determined experimentally in alluvium samples (Figure K-2). The  $K_d$  of  $^{237}\text{Np}$  and  $^{233}\text{U}$  in the alluvium differs from sample to sample depending on the depths and types of the tested alluvium. The  $K_d$  values range between 3 and 13 ml/g for  $^{237}\text{Np}$  and about 3 to 9 ml/g for  $^{233}\text{U}$ . The sorption capacity of alluvium for  $^{237}\text{Np}$  is larger than that for  $^{233}\text{U}$ .



00346DCc\_012

Source: DTNs: LA0302MD831341.003, LA0302MD831341.004.

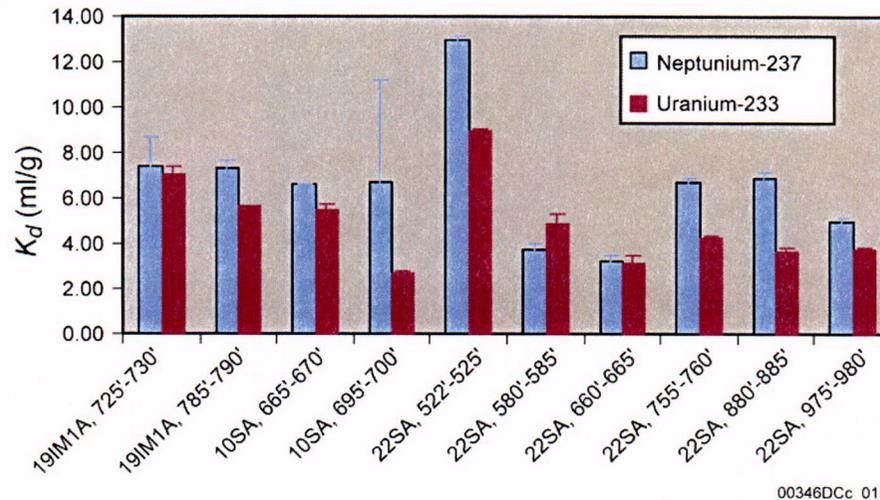
NOTE: Experiments terminated after two weeks. Liquid to solid ratio was 20 ml/g. NC-EWDP-19D Zone 1 water was used for the experiments with alluvium from NC-EWDP-19IM1A and NC-EWDP-22SA, and NC-EWDP-10S water was used for the experiments with alluvium from NC-EWDP-10SA.

Figure K-2.  $K_d$  Values for  $^{237}\text{Np}$  and  $^{233}\text{U}$  in Alluvium

### K.4.3 Uranium Sorption Behavior in Alluvium

#### K.4.3.1 Uranium Sorption Experiments

Sorption kinetics of  $^{233}\text{U}$  was measured in three alluvium samples (Table K-3). After 1 day of exposure, the amount of  $^{233}\text{U}$  adsorbed onto alluvium changed little during the remainder of the tests. Thus, the equilibration rate for the uranium sorption reaction is relatively fast (Figure K-3). Higher  $K_d$  values from the NC-EWDP-22SA sample may be the result of higher smectite and clinoptilolite content (Table K-3).

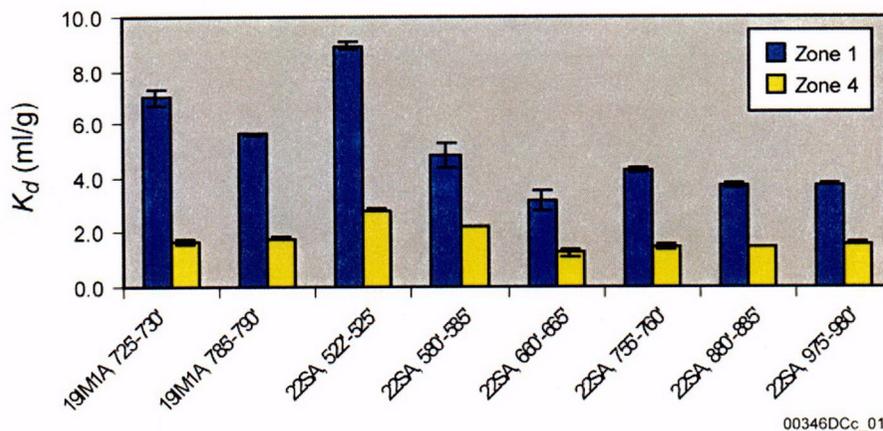


Source: Ding 2003, Attachment B.

NOTE: Liquid to solid ratio was 20 ml/g. NC-EWDP-19D Zone 1 water was used for the experiments with alluvium from NC-EWDP-19IM1A, and NC-EWDP-22SA, and NC-EWDP-10SA water was used for the experiments with alluvium from NC-EWDP-10SA.

Figure K-3. Batch  $K_d$  Values for  $^{233}\text{U}$  onto Alluvium as a Function of Time

To test if  $^{233}\text{U}$  sorption is a function of water composition, adsorption experiments were performed using water from NC-EWDP-19D Zones 1 and 4. The  $K_d$  values of  $^{233}\text{U}$  measured in Zone 4 water were lower than those for Zone 1 (Figure K-4). The major differences in these two waters (under the conditions of the laboratory experiments) were: the pH (Table K-1) and dissolved oxygen of Zone 4 water was higher than of Zone 1 water. The pH of the waters in the laboratory experiments were different from those measured in the field; the two waters had similar pH in the field, but the Zone 1 water decreased to a pH of 7.7 in the laboratory, and the water from Zone 1 increased to a pH of 9. The reasons for these differences in the changes in pH are not fully understood. The lower pH of the water from Zone 1 is likely a major cause for the higher sorption coefficients obtained in experiments using this water. The high pH of the Zone 4 water would have resulted in a large amount of carbonate ion ( $\text{CO}_3^-$ ) in this water, whereas the Zone 1 water would have had little carbonate ion present at a pH of 7.7. Uranium is known to form stable complexes with carbonate ion in solution (Langmuir 1997), so it would have been more likely to remain in solution at the higher pH of the Zone 4 water.



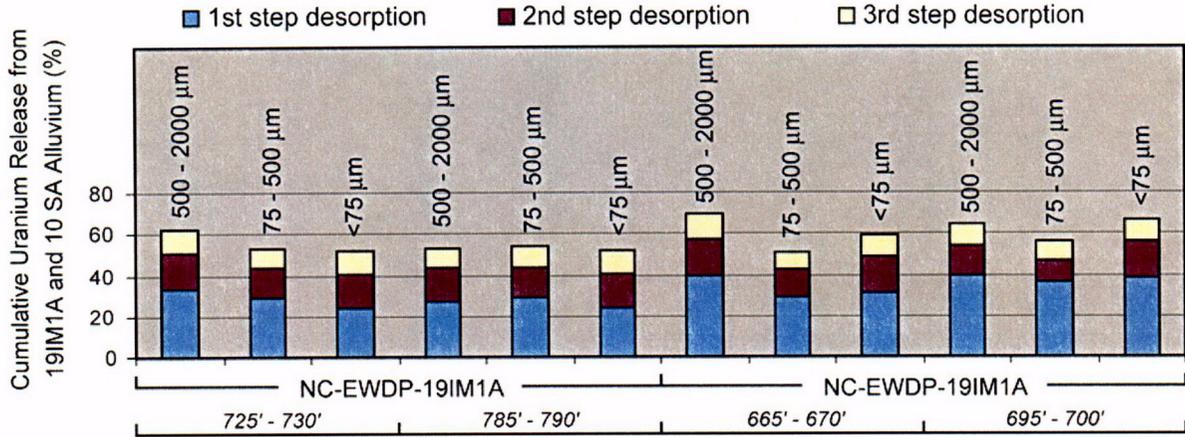
Source: DTN: LA0302MD831341.004

Figure K-4. Batch  $K_d$  Values for  $^{233}\text{U}$  in Water from Borehole NC-EWDP-19D, Zones 1 and Zone 4 Waters

#### K.4.3.2 Uranium Desorption Experiments

Multistep batch desorption experiments of  $^{233}\text{U}$  sorbed to alluvium were conducted (Figure K-5). Most of the uranium that desorbed did so during the first step. Less uranium desorbed in subsequent desorption steps. A large fraction (30 to 50 percent) of the sorbed  $^{233}\text{U}$  remained sorbed on the solid phase even after three desorption steps. These results suggest that the  $^{233}\text{U}$  desorption kinetics were relatively slow and that they may have been slowing as the experiments progressed.

Continuous-flow  $^{233}\text{U}$  desorption experiments were conducted after the end of some of the sorption experiments. The alluvium material containing sorbed  $^{233}\text{U}$  was removed from the test tubes used in the batch experiments and placed in a small "column" where it was then subjected to a continuous flow of water. The effluent from the column was analyzed for  $^{233}\text{U}$ . The results showed that the release of sorbed  $^{233}\text{U}$  slowed down after first 100 ml of groundwater had contacted the alluvium (Figure K-6), but release continued at a finite rate for the remainder of the experiment. The total duration of the experiment was about 5.5 days, including an approximately 2.5-day flow interruption just after 100 ml was eluted. The concentrations of eluted  $^{233}\text{U}$  near the end of the experiment were close to the detection limit. These results suggest that the desorption of sorbed  $^{233}\text{U}$  was slow. Simple linear extrapolation of the trends at the end of the experiments suggests that the total desorption after 3 weeks would be similar to the total desorption measured after 3 weeks in the multistep batch desorption experiments (Figure K-5).



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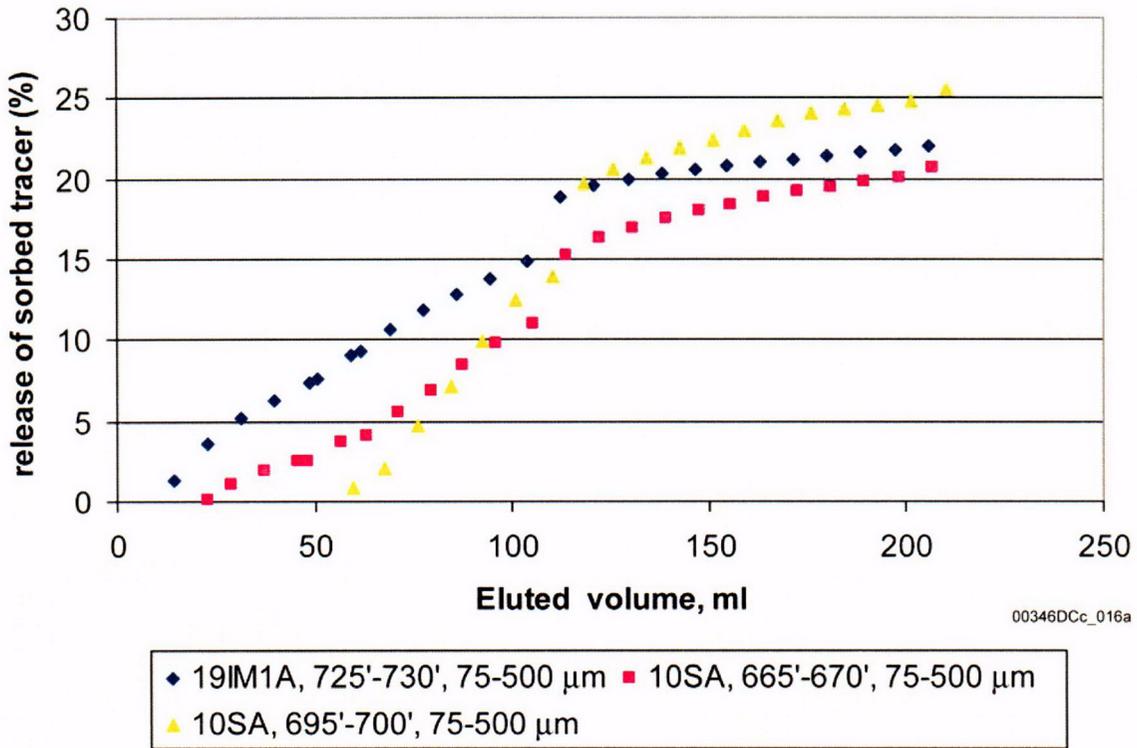
Source: Ding 2003, Attachment B.

NOTE: The time for each desorption step was one week. Liquid to solid ratio for desorption was about 20 ml/g.

Figure K-5. Cumulative Release of Sorbed <sup>233</sup>U from NC-EWDP-19IM1A and NC-EWDP-10SA Alluvium

### K.4.3.3 Uranium Column Experiments

Continuous-flow column experiments were conducted at room temperature and under ambient conditions at an elution rate of 10 ml/hr. The elution rate was decreased first to 5 ml/hr and then quickly to 3 ml/hr as the experiments progressed. Experimental conditions are presented in Table K-4. The <sup>233</sup>U breakthrough curves relative to tritium are shown in Figure K-7. In all cases, a small fraction of the uranium broke through at almost the same time as the tritium, but the majority of the uranium mass was retarded relative to the tritium. Total uranium recoveries ranged from 25 to 62 percent. The long tails and incomplete recoveries observed in the column experiments indicate that some of the <sup>233</sup>U was slow to desorb from the columns within the timeframe of the experiments. These experiments have not been interpreted to obtain estimates of uranium sorption parameters.



Source: Ding 2003, Attachment B.

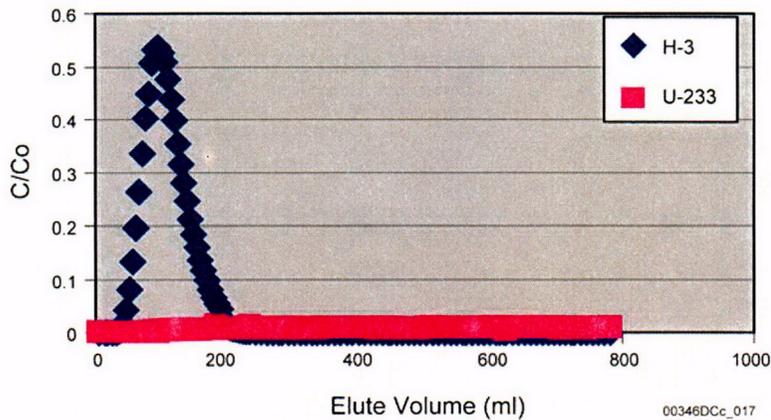
NOTE: Flow rate = 3 ml/h. Water from borehole NC-EWDP-19D Zone 1 was used for the NC-EWDP-19IM1A sample; water from borehole 10 S was used for the NC-EWDP-10SA samples.

Figure K-6. Release of Sorbed <sup>233</sup>U as a Function of Elute Volume of Groundwater

Table K-4. Experimental Conditions Uranium Columns

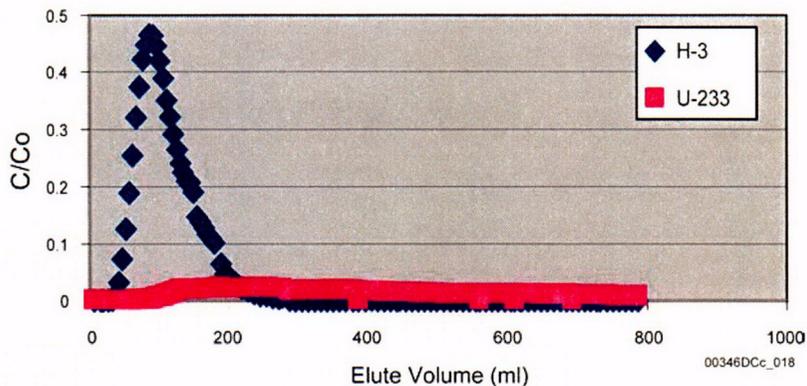
	Column 1	Column 2	Column 3
Geological Medium	19IM1A	10SA	22SA
Interval (below land surface)	725-730	665-670	522-525
Particle Size (μm)	75-2000	75-2000	75-2000
Water Used	19D Zone 1	10S	19D Zone 1
pH range	8.4-8.7	8.2-8.5	8.4-8.7
Diameter, cm	2.5	2.5	2.5
Dry alluvium packed in column (g)	374.61	356.59	390.72
Water weight after the saturation (g)	89.82	102.4	85.98
Porosity in column	0.41	0.44	0.39

Source: Ding 2003, Attachment B.



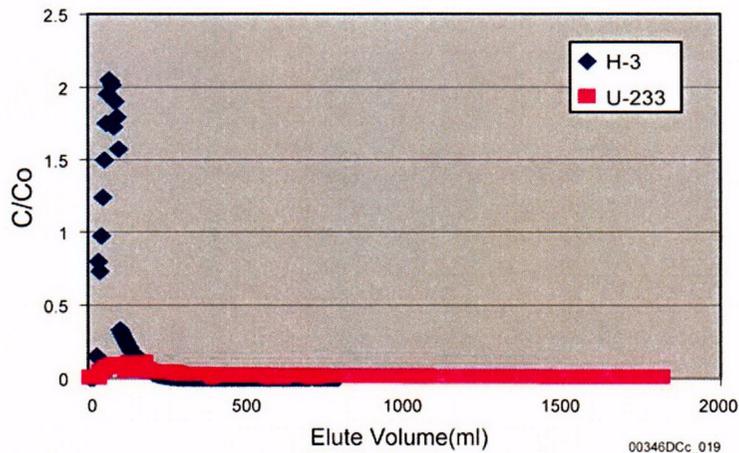
Source: Ding 2003.

Figure K-7a. Column 1, <sup>233</sup>U and Tritium Breakthrough Curves



Source: Ding 2003.

Figure K-7b. Column 2, <sup>233</sup>U and Tritium Breakthrough Curves



Source: Ding 2003.

NOTE: The total recovery of tritium was about 92 percent, and that of <sup>233</sup>U was about 65 percent. The flow rate was 10 ml/h.

Figure K-7c. Column 3, <sup>233</sup>U and Tritium Breakthrough Curves

## K.4.4 Neptunium Sorption Behavior in Alluvium

### K.4.4.1 Materials used in Early Neptunium Experiments

The alluvium materials used in the early neptunium experiments were obtained from different intervals in five boreholes (NC-EWDP-2D, NC-EWDP-9S, NC-EWDP-3S, NC-EWDP-1X, NC-EWDP-19D) located south of Yucca Mountain. The alluvium samples and preparation methods are presented in Table K-5.

Table K-5. Early Neptunium Experiment Boreholes and Sample Preparation Methods

Borehole Location	Depth (ft BLS)	Sample Preparation Method <sup>a</sup>	Particle Size Fraction (wt %)		
			75-2000 $\mu\text{m}$	75-500 $\mu\text{m}$	< 75 $\mu\text{m}$
2D	395-400	A	ND	59	41
2D	400-405	A	ND	60	40
2D	405-410	A	ND	56	44
2D	410-415	A	ND	56	44
9S	145-150	A	ND	66	34
9S	150-155	A	ND	62	38
9S	155-160	A	ND	61	39
9S	160-165	A	ND	61	39
3S	60-65	A	ND	54	46
3S	65-70	A	ND	64	36
3S	70-75	A	ND	59	41
3S	75-80	A	ND	66	44
1X	390-395	B+A	40	39	21
1X	395-400	B+A	71	19	10
1X	400-405	B+A	33	45	22
1X	405-410	B+A	51	33	16
19D	405-425	A	ND	ND	ND
19D	405-425	C	100	0	0
19D	405-425	C	0	0	100

Source: Ding et al. 2003.

NOTE: BLS = below land surface; ND = not determined.

<sup>a</sup> Sample Preparation Method: A) grind, crush, and dry sieve; B) collect 75-2000 $\mu\text{m}$  size particle materials by dry sieving without grinding or crushing, followed by process A; C) collect 75 to – 2,000  $\mu\text{m}$  size particle materials by dry sieving without grinding or crushing processes, follow with washing out the fine particles and collecting particle size range 75 to –2,000  $\mu\text{m}$  materials by wet sieving.

The water used in these experiments came from three locations (borehole NC-EWDP-03S and Zones 1 and 2 in borehole NC-EWDP-19D). The water compositions were similar (Table K-6) but water from borehole NC-EWDP-03S had a lower dissolved oxygen concentration, lower Eh, and a higher organic carbon concentration than water from NC-EWDP-19D. Thus, groundwater from borehole NC-EWDP-3S has more reducing conditions than groundwater from different zones in borehole NC-EWDP-19D.

Table K-6. Composition of Water from Boreholes NC-EWDP-03S and NC-EWDP-19D

Species	Concentration (mg/L)		
	3S (449 ft BLS)	19D1 (412-439 ft + 490-519 ft BLS)	19D2 (412-437 ft BLS)
Na <sup>+</sup>	141	69.4	73.2
K <sup>+</sup>	2.99	3.61	3.92
Li <sup>+</sup>	0.26	0.087	0.081
Ca <sup>2+</sup>	0.94 ± 0.01	7.59	7.70
Mg <sup>2+</sup>	0.14	0.65	0.69
Mn <sup>2+</sup>	< 0.002	0.0088	< 0.0001
Fe <sup>2+3+</sup>	0.02	0.09	< 0.01
Al <sup>3+</sup>	0.34	0.05	0.002
SiO <sub>2</sub>	48.4	58.0	58.4
F <sup>-</sup>	3.24	1.78	1.96
Cl <sup>-</sup>	8.68	5.61	6.52
NO <sub>3</sub> <sup>-</sup>	0.28	4.18	4.84
SO <sub>4</sub> <sup>2-</sup>	50.0	23.0	23.8
HCO <sub>3</sub> <sup>-</sup>	261	168	146
CO <sub>3</sub> <sup>2-</sup>	ND	0	17.9
Alkalinity (CaCO <sub>3</sub> )	193	ND	ND
PH	8.67	8.11	9.02
Eh (mv/SHE) <sup>a</sup>	190	ND	ND
DO	0.02	ND	ND
TOC	1.5	<0.6	0.67
Ionic strength (mol/kg)	0.007	0.004	0.005

Source: Ding 2003.

NOTE: ND = not determined; DO = dissolved oxygen; TOC = total organic carbon; SHE = standard hydrogen electrode.

<sup>a</sup> SHE is the reference electrode for reporting Eh data.  $Eh(SHE)_{\text{sample}} = Eh(SHE)_{\text{measured for sample}} + \{[(285-2.0) \times (T-25)] - Eh(SHE)_{\text{measured for 7.0 buffer}}\}$ .

Alluvium samples were characterized primarily using quantitative X-ray diffraction and N<sub>2</sub>-BET surface area measurements (Table K-7). Samples were selected from different borehole locations, intervals, sieving methods, and particle sizes.

The mineralogy of the alluvium used in the experiments is summarized in Table K-7. The amount of organic carbon in the samples was negligible. Trace amounts of calcite and hematite were detected in some samples. Alluvium from borehole NC-EWDP-03S contained a considerable amount of calcite. Dry sieved samples were used for all the experiments except for a column experiment with alluvium from NC-EWDP-19D. The sieving technique (wet versus dry) had a minor effect on the mineral composition of the 75 to 500 μm fraction of the 19D sample from borehole NC-EWDP-19D.

Table K-7. Mineral Abundance and Surface Areas for Selected Alluvium Samples used in Early Neptunium Sorption Tests

Alluvium				Quantitative mineral abundance for alluvium samples (wt percent)											Surface area (m <sup>2</sup> /g)	Organic Carbon (wt %)
Sieve Method	Bore-hole	Depth (ft BLS)	PS (μm)	Smec-tite	Clino-ptilolite	Kaol-nite	Mica	Tridy -mite	Cristo-balite	Quartz	Feld-spar	Calcite	Hema-tite	Total		
Dry	2D	410-415	75-500	2±1	4±1	1±1	trace	3±1	16±1	18±1	54±8	---	1±1	99±8	1.97	---
	9Sx	160-165	75-500	6±2	3±1	---	trace	1±1	18±1	14±1	58±8	---	trace	100±8	2.80	---
	3S	75-80	75-500	1±1	13±1	1±1	1±1	---	10±1	17±1	53±8	4±1	---	100±8	3.67	---
	19D	405-425	75-500	5±2	7±1	1±1	trace	3±1	13±1	20±2	52±8	trace	trace	101±9	7.60	0.22
	2D	410-415	< 75	4±1	7±1	1±1	1±1	5±1	14±1	17±1	53±8	---	1±1	103±8	4.27	---
	2D	395-400	<75	10±3	13±1	1±1	trace	4±1	13±1	11±1	47±7	1±1	trace	100±8	5.55	---
	9S	155-160	< 75	19±6	3±1	trace	1±1	4±1	14±1	12±1	50±7	---	trace	103±9	5.69	---
	3S	60-65	< 75	7±2	13±1	2±1	1±1	1±1	11±1	12±1	44±7	9±1	trace	100±8	11.94	---
Wet	19D	405-425	75-2000	4±1	5±1	1±1	1±1	3±1	16±1	16±1	49±7	---	1±1	96±8	5.42	0.15
	19D	405-425	< 75	48±14	6±1	1±1	1±1	2±1	5±1	8±1	29±4	1±1	---	101±15	73.65	0.76
	3S	65-70	< 75	30±9	21±2	1±1	2±1	trace	2±1	5±1	25±4	12±1	---	98±10	37.49	---

Source: Ding 2003, Attachment C.

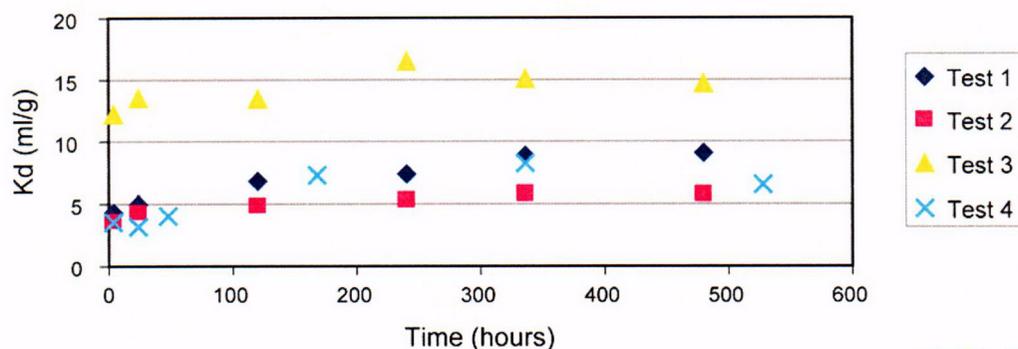
NOTE: PS = particle size; "—" = not detected; trace = amount at less than 0.5 weight percent. Surface area measurements were conducted using MONOSORB N<sub>2</sub>-BET Single Point Surface Area Analyzer.

#### K.4.4.2 Neptunium Batch Sorption Results from Early Experiments

**Kinetics of Neptunium(V) Interaction with Alluvium**—Kinetic experiments, using the experimental conditions described in Table K-8, were conducted to examine the interaction of neptunium(V) and alluvium. The initial sorption kinetics were fast (Figure K-8). After 1 day of exposure, the amount of neptunium(V) adsorbed onto alluvium changed little with time in all four tests. The effects of different waters and concentrations of neptunium(V) were not systematically evaluated, but they appeared to be less important than the alluvium characteristics.

Table K-8. Experimental Conditions for Kinetics of Neptunium(V) Interaction with Alluvium

Test	Alluvium			Neptunium(V) Initial Concentration	Water used
	Borehole	Depth (ft BLS)	Particle Size ( $\mu\text{m}$ )		
Test 1	2D	410-415	75-500	$1 \times 10^{-7}$ mol/L	NC-EWDP-3S
Test 2	9S	160-165	75-500	$1 \times 10^{-7}$ mol/L	NC-EWDP-3S
Test 3	3S	75-80	75-500	$1 \times 10^{-7}$ mol/L	NC-EWDP-3S
Test 4	19D	405-425	75-2000	$1 \times 10^{-6}$ mol/L	NC-EWDP-19D1

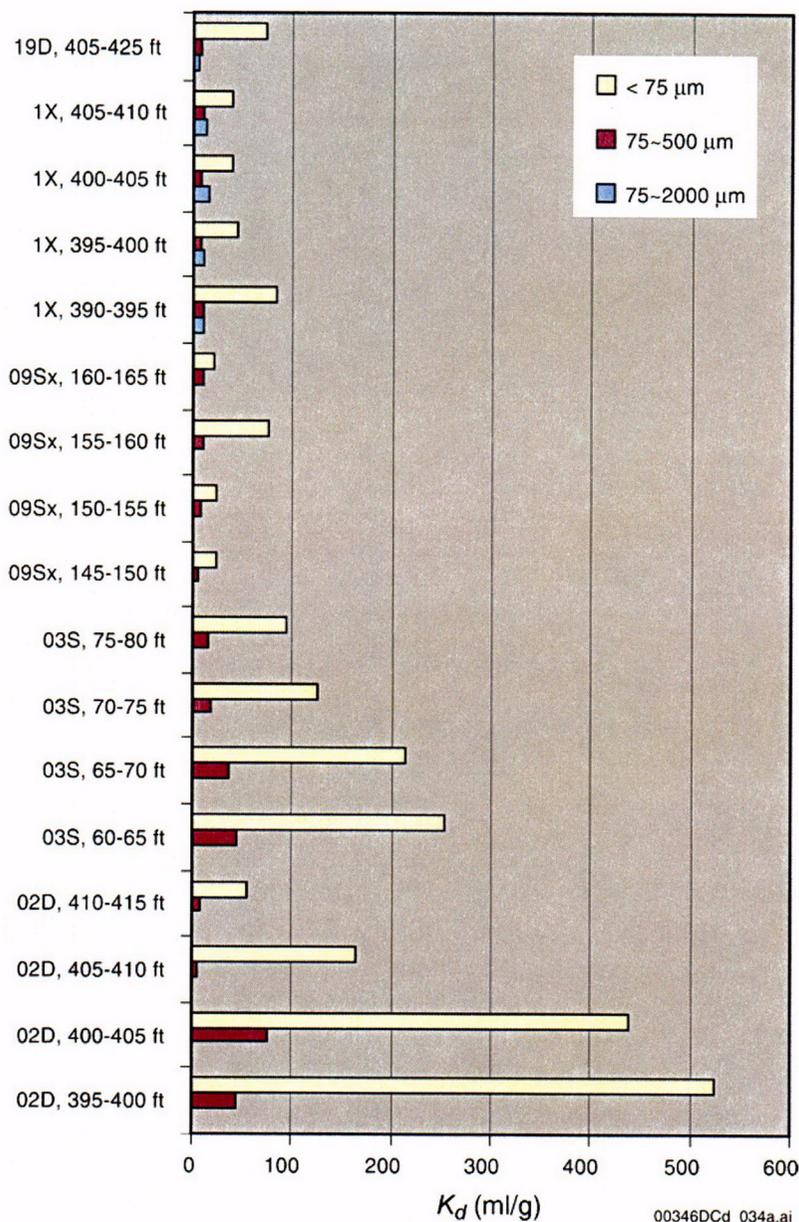


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Source: Ding 2003, Attachments A and C. DTN: LA0106MD831341.001.

Figure K-8. Sorption Kinetic of  $^{237}\text{Np}$  in Alluvium

**Range of  $K_d$  Values for Neptunium(V)**—The experimentally determined  $K_d$  values for all of the alluvium samples listed in Table K-5 are presented in Figure K-9. The experimental period for the tests was 2 weeks. Groundwater from borehole NC-EWDP-19D1 was used for NC-EWDP-19D alluvium test. Groundwater from borehole NC-EWDP-3S was used for all other experiments. The results suggest that the  $K_d$  of neptunium(V) in alluvium differs from sample to sample and ranges from about 4 to 500 ml/g. The particle size of the sample appears to be important with respect to the  $K_d$  value. In general, the smaller the particle size, the larger the  $K_d$  value. Alluvium samples from near the surface of boreholes NC-EWDP-2D and NC-EWDP-3S had a large adsorption capability for neptunium(V).

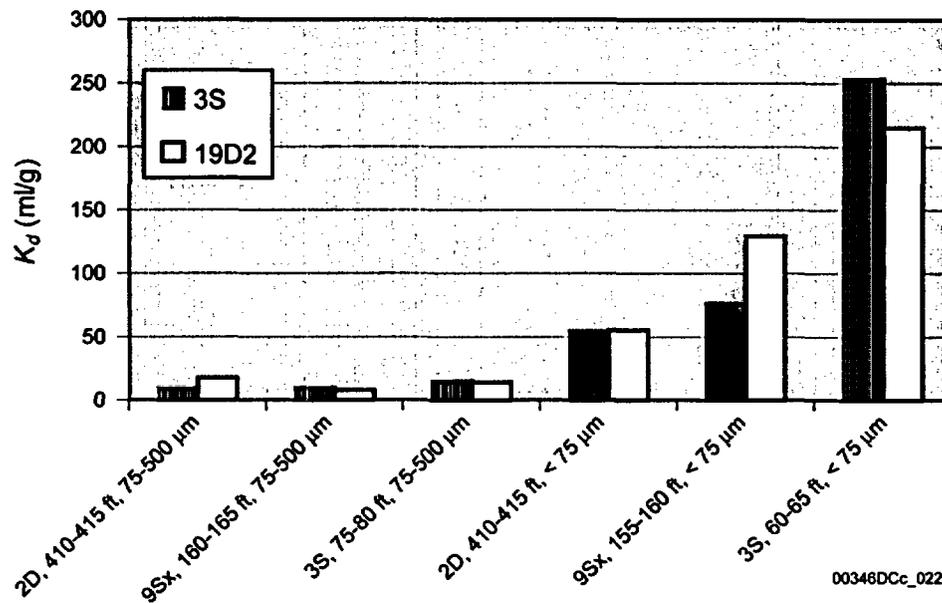


Source: Ding 2003, Attachments A and C.

Figure K-9. Batch  $K_d$  Values for Neptunium(V) in Different Intervals and Size Fractions

**Effect of Groundwater Chemistry on Neptunium(V)  $K_d$  Values**—Adsorption experiments were conducted using  $^{237}\text{Np}$  and alluvium and groundwater from the same boreholes (NC-EWDP-03S and NC-EWDP-19D). The  $K_d$  values obtained for a given sample with the two waters were similar (Figure K-10). Results from experiments using water from borehole NC-EWDP-03S were not used in developing  $K_d$  distributions for use in the site-scale saturated zone flow model.

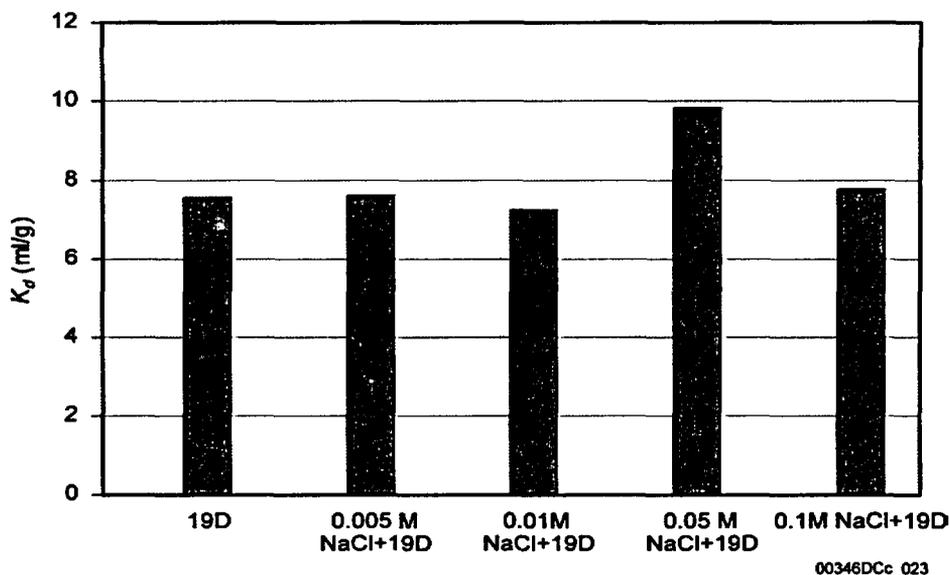
This result suggests that the different redox states of the two waters had little effect on neptunium sorption behavior or that the waters used in the experiments had equilibrated with the atmosphere before they were used.



Source: Ding 2003, Attachments A and C.

Figure K-10. Batch  $K_d$  Values for Neptunium(V) in Waters from Boreholes NC-EWDP-3S and NC-EWDP-19D

**Effects of Ionic Strength on  $^{237}\text{Np}$   $K_d$  Values**—The adsorption of  $^{237}\text{Np}$  in alluvium from borehole NC-EWDP-19D was examined under various ionic strengths. The original ionic strength of water from borehole NC-EWDP-19D was 0.004, but this was modified by adding sodium chloride. The  $K_d$  of  $^{237}\text{Np}$  changed little with increasing ionic strength (Figure K-11), suggesting that the reaction mechanism probably is dominated by surface complexation rather than ion exchange. An additional experiment (not shown) indicated a larger  $K_d$  value in deionized water than in the water from borehole NC-EWDP-19D, suggesting a possible role of carbonate in suppressing neptunium sorption in the water from borehole NC-EWDP-19D (carbonate was not present in the deionized water).



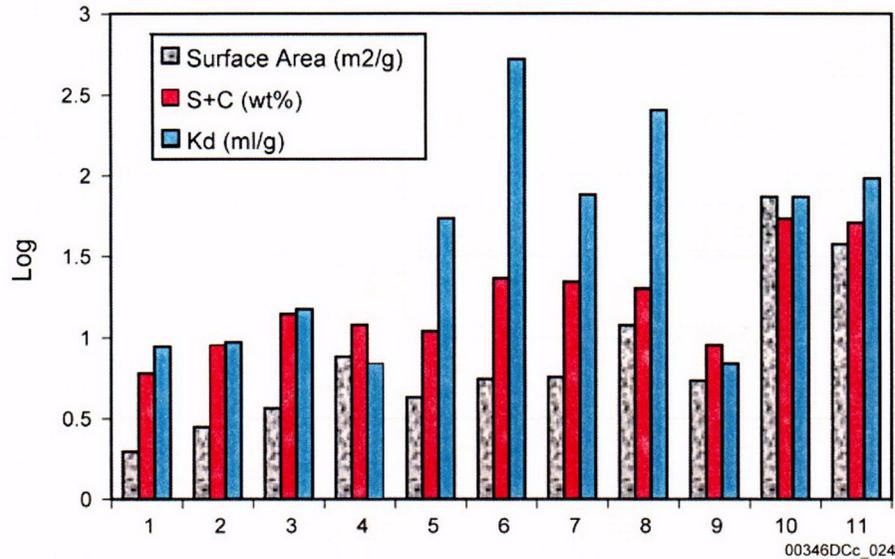
Source: Ding 2003, Attachments A and C.

Figure K-11. Batch  $K_d$  Values for  $^{237}\text{Np}$  in Solutions with Different Ionic Strengths

**Alluvium  $K_d$  Values in Relation to Surface Area and Secondary Mineral Content**—Surface reactions (e.g., sorption) depend on the surface properties of the geosorbents (e.g., surface area). The larger the surface area of the sample, the larger will be the  $K_d$  value obtained under the same experimental conditions. Clays and zeolites have larger surface areas than do primary minerals. Thus, alluvium containing more clay and zeolites would be expected to have larger  $K_d$  values.

Experiments were conducted to examine the relationships among surface area, the amount of secondary minerals (combined amounts of smectite and clinoptilolite), and the  $K_d$  values of  $^{237}\text{Np}$  in alluvium. The results of these experiments are presented in Figure K-12.

The surface area of the alluvium samples was related to the amount of smectite and clinoptilolite in the sample, such that the larger the amount of smectite and clinoptilolite, the larger the surface area. However, two samples with high  $K_d$  values did not have high smectite and clinoptilolite contents, and they did not have the highest surface areas. Thus, while neptunium sorption is positively correlated with surface area and mineralogy, trace amounts of minerals such as amorphous iron and manganese oxides, which were not identified by quantitative X-ray diffraction, may ultimately exert more influence on neptunium  $K_d$  values in the alluvium. Studies of sorption by neptunium, plutonium, and americium in the vitric tuffs of Busted Butte indicated that sorption increases with increasing levels of smectite, iron, and manganese oxides in the rock (Turin et al. 2002).



Source: Ding 2003, Attachments A and C.

Figure K-12. Surface Area, Combined Smectite and Clinoptilolite, and  $K_d$  Values for Neptunium(V)

#### K.4.4.3 Neptunium Column Transport Experiments

Two sets of column experiments were performed to investigate the transport behavior of neptunium(V) in saturated alluvium under flowing conditions. Experimental conditions for the two studies are listed in Tables K-9 and K-10. In all column experiments, tritium was used as the conservative tracer. Water from borehole NC-EWDP-03S was used in the column 1 experiment and water from NC-EWDP-19D was used in the experiments using columns 2 through 4. The latter experiments were reported by Ding et al. (2003).

Table K-9. Column Study (I)

	Column 1
Geological Medium	-03S
Interval (ft. BLS)	65-70
Particle Size ( $\mu\text{m}$ )	75-500
Water Used	-03S
pH range	8.5-9.0
Diameter, cm	1.0
Length of column (cm)	60
Porosity in column	0.45
Flow rate (ml/h)	2 (reduced to 0.5 ml/h late in the test)

Source: Ding 2003, Attachment A.

Table K-10. Column Study (II)

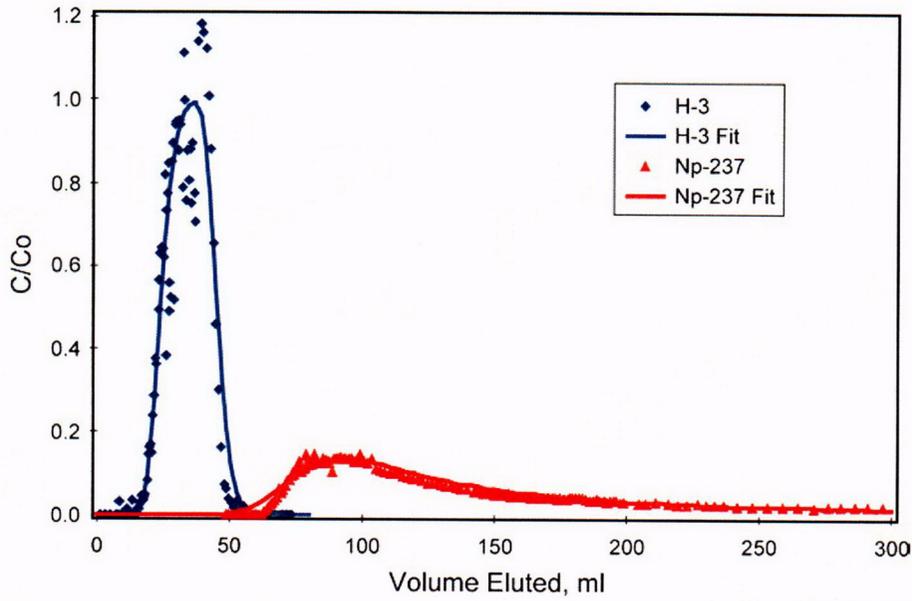
	Column 2	Column 3	Column 4
Geological Medium	-19D	-19D	-19D
Interval (ft. BLS)	405-425	405-425	405-425
Particle Size ( $\mu\text{m}$ )	75-2000	75-2000	75-2000
Water Used	19D	19D	19D
pH range	8.4-8.7	8.4-8.7	8.4-8.7
Diameter, cm	2.5	2.5	2.5
Length of alluvium in the column (cm)	45	45	45
Porosity in column	0.38	0.37	0.34
Flow rate (ml/h)	0.6	3	10
Np recovery (%)	NA	32	9

Source: Ding 2003, Attachment C.

**Results**—Figure K-13 shows the breakthrough curve of neptunium from column 1, and Figure K-14 shows the breakthrough curves of neptunium from columns 2, 3, and 4. There was no breakthrough of neptunium after about 12.5 pore volumes had been eluted in the 0.6 ml/hr test (Figure K-14). The  $K_d$  value corresponding to a breakthrough at 12.5 pore volumes is approximately 2.7 ml/g for the column in which this test was conducted. Thus, all of the neptunium in the 0.6 ml/hr test had an effective  $K_d$  value of greater than 2.7 ml/g. This test is important because the linear flow velocity in the column was 43 m/yr, which is consistent with estimates of linear flow velocities in the alluvial aquifer (10 to 80 m/yr) (BSC 2003).

Higher flow rates result in a lower effective  $K_d$  value for at least a portion of the neptunium traveling through the columns (Figure K-14). However, despite the early breakthroughs in the experiments at the two higher flow rates, the recoveries of neptunium were low (32 percent or less), suggesting slow desorption rates for most of the neptunium in the columns. Furthermore, the long tails in these experiments suggest a wide range of desorption rates for neptunium. The minimum possible  $K_d$  value in the lowest flow rate column test (2.7 ml/g) agrees better with the batch studies ( $K_d = 6.9$  ml/g) than the  $K_d$  values for the earliest arriving neptunium in the higher flow rate tests.

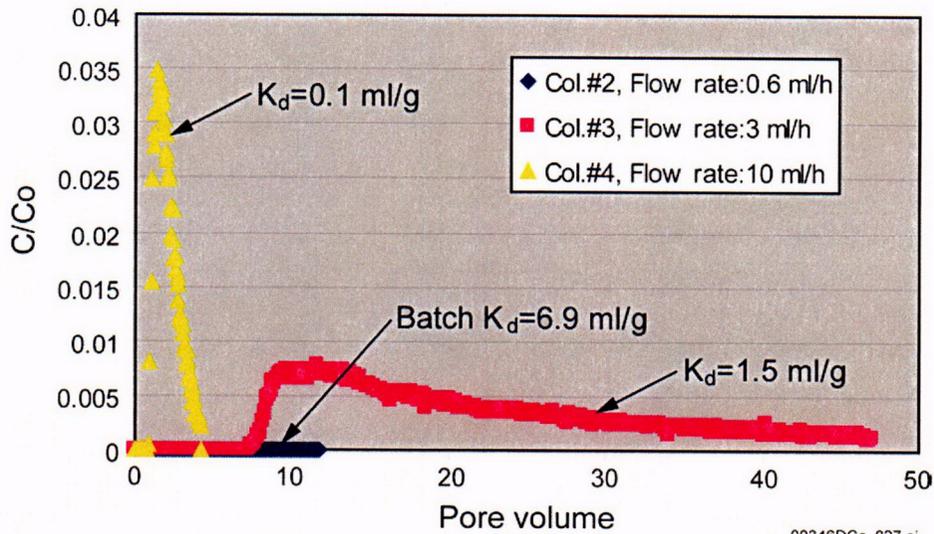
The observed differences in neptunium transport as a function of flow rate cannot be explained by a single rate-limited sorption reaction. A dual-porosity model was used to model the data of Figure K-13 after a single-porosity kinetic sorption model could not provide a reasonable fit. A good fit by the dual-porosity model in this case is not taken to imply that there was a large amount of stagnant water in the columns with which the flowing water is in diffusive communication. Rather, this result was taken to indicate that there may be a mass transport step occurring in series with a sorption reaction in the column. However, the column results could also be explained by multiple sorption reactions occurring at different rates and with different effective  $K_d$  values (because of different sorption sites). Preliminary modeling of the column experiments (Figure K-14) suggests that the latter explanation is more consistent with the results. The column experiments reveal that reactive transport processes in heterogeneous alluvium, even at a relatively small scale, are complicated and not amenable to simple transport models, at least when flow velocities are high.



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Source: Ding 2003, Attachment A.

Figure K-13. Neptunium and Tritium Breakthrough Curves in Column 1



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Source: Ding 2003, Attachment C.

Figure K-14. Neptunium Breakthrough Curves for Columns 2 and 3

## K.5 REFERENCES

### K.5.1 Documents Cited

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Turin, H.J.; Groffman, A.R.; Wolfsberg, L.E.; Roach, J.L.; and Strietelmeier, B.A. 2002. "Tracer and Radionuclide Sorption to Vitric Tuffs of Busted Butte, Nevada." *Applied Geochemistry*, 17, (6), 825-836. New York, New York: Elsevier. TIC: 254046.

### K.5.2 Data, Listed by Data Tracking Number

GS011108312322.006. Field and Chemical Data Collected between 1/20/00 and 4/24/01 and Isotopic Data Collected between 12/11/98 and 11/6/00 from Wells in the Yucca Mountain Area, Nye County Nevada. Submittal date: 11/20/2001.

LA0106MD831341.001. Adsorption of Np-237 in Three Types of Alluvium as a Function of Time and Stratigraphic Position. Submittal date: 06/21/2001.

LA0206AM831234.002. Geochemical Field Measurements on Nye County EWDP Wells. Submittal date: 06/21/2002.

LA0302MD831341.001. Iodine-129 Sorption in Alluvium from NC-EWDP Wells 19IM1A, 10SA, and 22SA under Ambient Conditions. Submittal date: 02/13/2003.

LA0302MD831341.002. Technetium-99 Sorption in Alluvium from NC-EWDP Wells 19IM1A, 10SA, and 22SA under Ambient Conditions. Submittal date: 02/11/2003.

LA0302MD831341.003. Neptunium-237 Sorption in Alluvium from NC-EWDP Wells 19IM1A, 10SA, and 22SA under Ambient Conditions. Submittal date: 02/11/2003.

LA0302MD831341.004. Uranium Sorption in Alluvium from NC-EWDP Wells 19IM1A, 10SA, and 22SA Under Ambient Conditions. Submittal date: 02/11/2003.

**APPENDIX L**  
**TRANSPORT—TEMPORAL CHANGES IN HYDROCHEMISTRY**  
**(RESPONSE TO TSPA I 3.31)**

### **Note Regarding the Status of Supporting Technical Information**

This document was prepared using the most current information available at the time of its development. This Technical Basis Document and its appendices providing Key Technical Issue Agreement responses that were prepared using preliminary or draft information reflect the status of the Yucca Mountain Project's scientific and design bases at the time of submittal. In some cases this involved the use of draft Analysis and Model Reports (AMRs) and other draft references whose contents may change with time. Information that evolves through subsequent revisions of the AMRs and other references will be reflected in the License Application (LA) as the approved analyses of record at the time of LA submittal. Consequently, the Project will not routinely update either this Technical Basis Document or its Key Technical Issue Agreement appendices to reflect changes in the supporting references prior to submittal of the LA.

## APPENDIX L

### TRANSPORT—TEMPORAL CHANGES IN HYDROCHEMISTRY (RESPONSE TO TSPA I 3.31)

This appendix provides a response for Key Technical Issue (KTI) agreement Total System Performance Assessment and Integration (TSPA I) 3.31. This KTI agreement relates to providing more information about effects in temporal changes in water chemistry on transport parameters.

#### L.1 KEY TECHNICAL ISSUE AGREEMENT

##### L.1.1 TSPA I 3.31

KTI agreement TSPA I 3.31 was reached during the U.S. Nuclear Regulatory Commission (NRC)/U.S. Department of Energy (DOE) TSPA I technical exchange and management meeting on total system performance assessment and integration held August 6 through 10, 2001, in Las Vegas, Nevada. TSPA I KTI subissues 1, 2, 3, and 4 were discussed at that meeting (Reamer 2001).

During the technical exchange (Reamer 2001), the NRC and the DOE discussed NRC comments pertaining to radionuclide transport in the saturated zone model abstraction. The NRC asked if changes in radionuclide concentration in the saturated zone model used in the total system performance assessment changes as a result of the inclusion of FEP 2.2.08.01.00, Groundwater Chemistry/Composition in Unsaturated Zone and Saturated Zone. The DOE responded that the code did not simulate changes in radionuclide concentration in the saturated zone. Individual realizations included spatially variable  $K_d$  values only through the distinction between volcanic and alluvium units, but temporally constant  $K_d$  values. The NRC expressed concern that the total system performance assessment code would not show potential increases in dose if  $K_d$  values decrease in the future.

Wording of the agreement is:

##### TSPA I 3.31<sup>1</sup>

Evaluate the effects of temporal changes in saturated zone chemistry on radionuclide concentrations (SZ2.3.2).

DOE will reexamine the FEPs, currently included in the performance assessment, that may lead to temporal changes in saturated zone hydrochemistry. If the DOE determines that these FEPs can be excluded, the results will be documented in the FEP Saturated Zone Flow and Transport AMR (ANL-NBS-MD-000002) in FY 2003. If the DOE determines that these FEPs cannot be excluded from the performance assessment, the DOE will evaluate the effects of temporal changes in the saturated zone chemistry on radionuclide concentrations and will document this evaluation in above-mentioned AMR.

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<sup>1</sup> SZ2.3.2 in this agreement refers to NRC integrated subissue SZ 2 (NRC 2002, Table 1.1-2).

### **L.1.2 Related Key Technical Issue Agreements**

None.

## **L.2 RELEVANCE TO REPOSITORY PERFORMANCE**

The subject of the agreement is the further evaluation of the effects of temporal changes in water chemistry on radionuclide concentrations. This is directly relevant to the output of the site-scale saturated zone flow model, and therefore, to the performance assessment. Adequate characterization of saturated zone transport is required by 10 CFR Part 63 (66 FR 55732).

Retardation of radionuclides by sorption is an important component of the saturated zone performance, and the geochemical processes potentially affecting radionuclide sorption must be fully evaluated. Temporal changes in saturated zone chemistry that might alter sorption and the transport of radionuclides require evaluation. Analysis of the potential effects of temporal changes in saturated zone chemistry on the determination of sorption coefficients is provided in this appendix, and the treatment of these potential effects in the total system performance assessment is identified and discussed.

### **L.3 RESPONSE**

The effects of temporal changes in saturated zone chemistry on radionuclide concentrations have been evaluated. Temporal changes in saturated zone chemistry could include changes in rock chemistry, changes in water chemistry, or changes in both. The evaluation indicated that the effects relating to potential changes in rock chemistry have been included in the total system performance assessment through the sorption coefficient probability density functions. The effects of changes in water chemistry through changes in major ion concentrations and in pH similarly have been accounted for in the sorption coefficient probability density functions. Potential changes in Eh and dissolved oxygen have not been incorporated into the probability density functions. Probability density functions were derived under the assumption that conditions in the flow system are oxidizing, which leads to more rapid radionuclide transport than reducing conditions.

However, concern has been expressed regarding the potential effect of transient reducing conditions. The potential for transient reducing conditions to occur has been examined. It was concluded that such conditions may occur, but they are unlikely to have large effect on radionuclide transport. Reducing conditions could retard radionuclides increasing the sorption properties. We assume oxidizing conditions over the regulatory period which allows the radionuclides of interest to remain in solution, therefore able to be transported. Consequently, this scenario has been discounted. A scenario in which existing reducing conditions are altered during the regulatory time frame is considered more likely and has been evaluated. Locations have been examined where water quality data indicate that reducing conditions currently exist. Some of these locations are not in the potential flow paths from the repository, and one is suspected of being affected by drilling operations. Reducing conditions in areas affected by drilling are expected to dissipate. However, at least one of the locations is in the potential flow path and probably is not influenced by drilling operations. The reducing conditions at these locations appear to be due to natural processes. Thus, the most likely temporal changes in

saturated-zone chemistry are included in the total system performance assessment, while changes thought to be unlikely are not included in the total system performance assessment. For this reason, the main text of this report does not specifically include a discussion of temporal changes in hydrochemistry.

The information in this report is responsive to agreement TSPA 3.31 made between the DOE and NRC. The report contains the information that DOE considers necessary for the NRC to review for closure of this agreement.

#### **L.4 BASIS FOR THE RESPONSE**

Temporal changes in saturated zone chemistry could include changes in rock chemistry, changes in water chemistry, or both. The potential effect of such changes would primarily be on the sorption behavior of radionuclides. In general, the possible changes in rock chemistry could result in changes in the detailed distribution of retardation potential in the flow system. However, such changes would not change the net retardation potential in the flow system. Potential changes in rock chemistry that could affect the transport behavior of radionuclides primarily are changes in ion exchanger compositions (e.g., clays and zeolites) and changes in mineral surface compositions. Variation in ion exchanger compositions and mineral surface compositions were built into the sorption coefficient probability density functions used in the total system performance assessment (BSC 2003a, Attachment 1). More specifically, the probability density functions are based on sorption coefficient data obtained on rock samples taken from different locations on Yucca Mountain. For example, zeolitic samples used in laboratory experiments to obtain sorption coefficients reflect a range of zeolite compositions (Broxton et al. 1986). Similarly, laboratory experiments on devitrified or vitric tuffs used samples from different locations within Yucca Mountain in an attempt to sample the variation in surface chemical heterogeneities. To be conservative, the derived probability density functions are biased toward data on rock samples that primarily contain (greater than 95 percent) the major mineral phases or glass (e.g., feldspar, silica phases, zeolite, and glass; BSC 2003a, Attachment 1).

Temporal changes in water chemistry could include changes in the major ion concentrations as well as changes in pH, Eh, dissolved oxygen, and organic carbon content. Potential changes in major ion concentrations are included in the sorption coefficient probability density functions (BSC 2003a, Attachment 1). Two end-member water compositions were used in laboratory experiments to obtain sorption coefficients. These two water compositions (from boreholes UE-25 J-13 and UE-25 p#1) are considered to bracket the range in water compositions expected along potential flow paths in the saturated zone over the next 10,000 years. Basically, water from borehole UE-25 J-13 is used to represent the average composition of saturated zone waters. Although water that infiltrated during glacial times may be more dilute than water from borehole UE-25 J-13, the differences in the major ion compositions of these waters are small (e.g., the concentration of Cl<sup>-</sup> in glacial-aged groundwater ranges from 5 to 6.5 mg/L, while young groundwater in borehole UE-29 a#2 has a Cl<sup>-</sup> concentration of 8.3 mg/L; BSC 2003b).

The water composition in the volcanic portion of borehole UE-25 p#1 (BSC 2003b) was used to bracket unsaturated zone pore waters that may percolate into the saturated zone beneath Yucca Mountain and possible upward flow from the Paleozoic aquifer into the shallow saturated zone.

Because these waters are unlikely to comprise a major percentage of the flow along potential radionuclide pathways, the results of sorption experiments with these waters are given less emphasis in the derivation of the probability density functions.

Potential changes in pH are included in the probability density functions. Laboratory sorption coefficient experiments were carried out over a range of pH values, 6.8 to 8.6 (BSC 2003a, Attachment 1). Thus, by using the results of these experiments in the derivation of the probability density functions, the potential impacts of pH variations were addressed. The effects of variation in the organic content of saturated zone waters were addressed in experiments using waters from the site. These waters contain small amounts of dissolved organic matter (DTN: GS980908312322.008). Thus, using these waters in laboratory experiments allows the effect of dissolved organic matter to be included in the probability density functions.

Potential temporal changes in Eh and dissolved oxygen were not incorporated in the probability density functions. The probability density functions were derived under the assumption that conditions in the flow system will be oxidizing. The laboratory experiments on which the probability density functions are based were carried out in contact with atmospheric oxygen (BSC 2003a, Attachment 1). Thus, the results of these experiments reflect oxidizing conditions. In general, oxidizing conditions lead to more rapid radionuclide transport in the saturated zone than reducing conditions (Langmuir 1997, p. 485). However, the NRC has pointed out that the assumption that conditions are oxidizing might lead to dose dilution. In particular, it was pointed out that transient-reducing conditions in some part of the flow field could lead to the accumulation of some radioelements (e.g., neptunium, plutonium, technetium, and uranium). A subsequent return to oxidizing conditions within the regulatory time frame could result in enhanced groundwater concentrations of these radioelements. In the following discussion, it is concluded that transient reducing conditions are unlikely to develop during the regulatory time frame.

Possible scenarios in which transient reducing conditions might occur in the flow field include anthropogenic inputs (e.g., from sewage treatment plants, landfills, dairy farms, and leaks from tanks containing petroleum products). Because the land above the potential flow paths will be under deed restrictions (i.e., not part of the accessible environment), these potential sources of transient reducing conditions need not be considered further. Even in the absence of deed restrictions, the potential effect of anthropogenic inputs would be limited by the areal extent of the inputs relative to the width of the radionuclide flowfield. Transient reducing conditions also could be imposed from below the potential flow paths by the upward migration of hydrocarbons (e.g., methane) from the deep saturated zone. However, the hydrocarbon potential for the Yucca Mountain region is classified as low (French 2000), and therefore this scenario is discounted.

A more likely scenario involving reducing conditions is one in which the reducing conditions are not transient. Some groundwaters in deep boreholes at Yucca Mountain (e.g., USW H-1, USW H-3, USW H-4, and UE-25 b#1) and shallow boreholes directly east of Yucca Mountain (UE-25 WT-#17) currently show reducing conditions (BSC 2003a). In addition, some of the Nye County boreholes (NC-EWDP-1DX, NC-EWDP-3D, NC-EWDP-5S) also contain groundwaters that show reducing conditions. Table K-2 in Appendix K provides redox measurements in groundwater in Nye County boreholes.

The reducing conditions observed in deep boreholes such as USW H-3 (Ogard and Kerrisk 1984) are likely due to the presence of reducing agents in the aquifer matrix. The main reducing agent appears to be pyrite, although biotite and other ferrous-iron-bearing minerals may contribute to the reduction capacity of the aquifer matrix. In borehole USW H-3, pyrite is found deep in the Tram Tuff of the Crater Flat Group (Thordarson et al. 1984). Pyrite is present in the Tram Tuff as a primary (i.e., volcanic) constituent (Castor et al. 1994). Sufficient pyrite remains in the Tram member to provide substantial reducing capacity in this member over the regulatory time-frame. Thus, these reducing conditions are unlikely to be transient in a 10,000-year time frame.

Flow modeling (BSC 2003c) has shown that potential radionuclide flow paths are primarily through the Prow Pass and Bullfrog members of the Crater Flat Group. The Tram Tuff is located directly beneath the Bullfrog member. Thus, according to the flow model, radionuclides released from the repository will not come into contact with the reducing conditions in the Tram Tuff. Mineralogical analyses of samples from the Prow Pass and Bullfrog members of the Crater Flat Group from boreholes in the Yucca Mountain area do not indicate the presence of (CRWMS M&O 2000). Thus, it is unlikely that reducing conditions of the type found at borehole USW H-3 will be generated in the volcanic units through which radionuclides will be transported in the vicinity of Yucca Mountain.

Groundwater pumped from borehole UE-25 WT#17 showed reducing characteristics (Eh less than 0.0 mV, little or no dissolved oxygen and nitrate, high organic carbon), which were maintained over a pumping interval during which more than 4,000 gallons were pumped (DTN: LA0206AM831234.001). Analyses of the waters showed that organic carbon concentrations were unusually high (up to 20 mg/L; DTN: GS980908312322.008) for a borehole in volcanic rocks. One explanation for these observations is that drilling fluids containing organic materials were left in the borehole (i.e., the borehole was not properly developed). These fluids may have migrated in a downgradient direction from the borehole but were eventually drawn back into the borehole by the pumping event. This scenario would explain the low Eh, the low dissolved oxygen and nitrate concentrations, and particularly the high organic carbon concentrations. If this explanation is correct, the reducing conditions at this location should dissipate as groundwater containing the drilling fluid moves downgradient. An alternative explanation for the reducing conditions in borehole UE-25 WT#17 is that the site is located above a source of hydrocarbons in the deeper saturated zone (i.e., the Paleozoic aquifer). However, Yucca Mountain is considered to be an area with low hydrocarbon potential (French 2000), and this possibility is excluded or at least minimized.

Groundwater pumped from the Bullfrog Member in borehole UE-25 b#1 also showed reducing conditions (Ogard and Kerrisk 1984). Water pumped during the fourth day of pumping was more reducing than the water pumped during the 28th day (Eh = -18 versus 160 mv/SHE; dissolved oxygen = 0.6 versus 2.2 mg/L; nitrate = 2.2 versus 4.5 mg/L). After 28 days of pumping, the borehole was thought to be cleared of drilling fluids and the organic carbon concentration was reported to be only 0.55 mg/L (Ogard and Kerrisk 1984). This is a higher concentration than observed in water from well UE-25 J-13 (0.15 mg/L), but it is consistent with the reducing conditions, observed in UE-25b#1, and it is lower than the value of 20 mg/L observed in UE-25 WT-#17. Thus, in this case, the reducing conditions appear to be due to natural processes. A likely cause for these reducing conditions is flow from the Tram member

upgradient into the Bullfrog member downgradient at UE-25b#1. If this is the cause, the reducing conditions will persist over the regulatory time frame.

Reducing conditions have been observed in the alluvial aquifer in boreholes located east and west of Fortymile Wash (e.g., NC-EWDP-5SB, NC-EWDP-1DX, NC-EWDP-3S; (DTN: LA0206AM831234.002). The cause of reducing conditions in groundwater from borehole NC-EWDP-5SB is not clear. For boreholes NC-EWDP-1DX and NC-EWDP-3S, the reducing conditions likely reflect the presence of pyrite. Pyrite may be present in borehole NC-EWDP-5SB, but was not noted in the borehole cuttings. To the extent that the reducing conditions in these boreholes are maintained over the regulatory time frame, redox-sensitive radionuclides will be strongly retarded over the regulatory time frame along flow paths along the eastern and western edges of the potential flow field. Assuming the presence of pyrite is the main cause of reducing conditions in the alluvium, these conditions are expected to be present over the regulatory time frame.

In summary, the effects of temporal changes in saturated zone chemistry on radionuclide concentrations have been evaluated. The evaluation indicated that effects relating to changes in rock chemistry are included in the total system performance assessment through the sorption coefficient probability density functions used in the total system performance assessment. The effects of changes in water chemistry through changes in major ion concentrations and in pH also were accounted for in the sorption coefficient probability density functions. Potential changes in Eh and dissolved oxygen were not incorporated into the probability density functions. Probability density functions were derived under the assumption that conditions in the flow system are oxidizing, which leads to more rapid radionuclide transport than reducing conditions.

## L.5 REFERENCES

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### **L.5.2 Codes, Standards, Regulations, and Procedures**

66 FR 55732. Disposal of High-Level Radioactive Wastes in a Proposed Geologic Repository at Yucca Mountain, NV. Final Rule 10 CFR Part 63. Readily available.

### **L.5.3 Data, Listed by Data Tracking Number**

GS980908312322.008. Field, Chemical, and Isotopic Data from Precipitation Sample Collected Behind Service Station in Area 25 and Ground Water Samples Collected at Boreholes UE-25 C #2, UE-25 C #3, USW UZ-14, UE-25 WT #3, UE-25 WT #17, and USW WT-24, 10/06/97 to 07/01/98. Submittal date: 09/15/1998.

LA0206AM831234.001. Eh-pH Field Measurements on Nye County EWDP Wells. Submittal date: 06/21/2002.

LA0206AM831234.002. Geochemical Field Measurements on Nye County EWDP Wells. Submittal date: 06/21/2002.

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**APPENDIX M**  
**MICROSPHERES AS ANALOGS**  
**(RESPONSE TO RT 3.08 AIN-1 AND GEN 1.01 (COMMENTS 43 AND 45))**

### **Note Regarding the Status of Supporting Technical Information**

This document was prepared using the most current information available at the time of its development. This Technical Basis Document and its appendices providing Key Technical Issue Agreement responses that were prepared using preliminary or draft information reflect the status of the Yucca Mountain Project's scientific and design bases at the time of submittal. In some cases this involved the use of draft Analysis and Model Reports (AMRs) and other draft references whose contents may change with time. Information that evolves through subsequent revisions of the AMRs and other references will be reflected in the License Application (LA) as the approved analyses of record at the time of LA submittal. Consequently, the Project will not routinely update either this Technical Basis Document or its Key Technical Issue Agreement appendices to reflect changes in the supporting references prior to submittal of the LA.

## APPENDIX M

### MICROSPHERES AS ANALOGS (RESPONSE TO RT 3.08 AIN-1 AND GEN 1.01 (COMMENTS 43 AND 45))

This appendix provides a response for additional information needed (AIN) request for Key Technical Issue (KTI) agreements Radionuclide Transport (RT) 3.08 and General Agreement (GEN) (1.01) Comments 43 and 45. These KTI agreements relate to providing more information about the justification for the use of carboxylate-modified latex (CML) polystyrene microspheres as analogs for natural colloids.

#### M.1 KEY TECHNICAL ISSUE

##### M.1.1 RT 3.08 AIN-1 and GEN 1.01 (Comments 43 and 45)

KTI agreement RT 3.08 was reached during the U.S. Nuclear Regulatory Commission (NRC)/U.S. Department of Energy (DOE) technical exchange and management meeting on radionuclide transport held December 5 through 7, 2000, in Berkeley, California. Radionuclide transport KTI subissues 1, 2 and 3 were discussed at that meeting (Reamer and Williams 2000). At the meeting, DOE indicated that they had completed tests at the C-Wells complex using microspheres, which will be used as part of the basis for justifying the use of microspheres as analogs for natural colloids. DOE considered these tests to be representative of transport for colloids. This discussion resulted in KTI agreement RT 3.08.

During the NRC/DOE technical exchange and management meeting on thermal operating temperatures, held September 18 through 19, 2001, the NRC provided additional comments relating to this RT KTI agreement (Reamer and Gil 2001). Those comments relating to microspheres as analogs resulted in KTI agreement GEN 1.01, Comments 43 and 45. DOE provided initial responses to these comments (Reamer and Gil 2001).

A letter report responding to agreement RT 3.08 (Ziegler 2002) was submitted. Specific additional information was requested by the NRC after the staff's review of this letter report was completed, resulting in RT 3.08 AIN-1 (Schlueter 2002). The NRC response to the letter report states that DOE needs to provide a stronger technical basis and adequate experimental evidence to indicate that CML microspheres can be used as analogues for colloids in alluvium. In addition, NRC stated that the DOE response to the agreement did not address GEN 1.01 (Comment 45), as discussed during the September 18 to 19 technical exchange.

As indicated by the associated NRC comments and responses that tie those comments to RT 3.08 (Reamer and Gil 2001), GEN 1.01 Comments 43 and 45 are addressed implicitly through the response to KTI agreement RT 3.08 AIN-1.

Wording of the agreements is:

##### RT 3.08

Provide justification that microspheres can be used as analogs for colloids (for example, equivalent ranges in size, charge, etc.). DOE will provide

documentation in the C-Wells AMR to provide additional justification that microspheres can be used as analogs for colloids. The C-Wells AMR will be available to the NRC in October 2001.

#### **RT 3.08 AIN-1**

1. Provide a stronger technical basis and adequate experimental evidence to indicate that CML microspheres can be used as analogs for colloids in alluvium.
2. Provide a response to General Agreement 1.01 (#45) to address the potential for remobilization of microspheres and/or colloids.

#### **GEN 1.01 (Comment 43)**

The Supplemental Science and Performance Analyses presents a new distribution for retardation of colloids with irreversibly attached radionuclides. The distribution takes into account new site-specific alluvium data. However, any future use of this distribution in Total System Performance Assessment (TSPA) will require comparison with results of field and laboratory tests. This concern is indirectly related to agreement TSPA1.3.30.

#### **DOE Initial Response to GEN 1.01 (Comment 43)**

DOE acknowledges that any future use of this distribution in TSPA will require comparison with results of field and laboratory tests. This concern is indirectly related to KTI agreements RT 3.07 and RT 3.08. Laboratory testing of microsphere and silica colloid retardation in alluvium-packed columns is in progress. Microspheres will be used as colloid tracers in alluvial testing complex cross-hole tracer testing.

#### **GEN 1.01 (Comment 45)**

In discussing preliminary microsphere transport tests at the Alluvial Testing Complex, it is mentioned that flow transients can remobilize microspheres. Is such a process possible in the repository system? If so, how can it be accommodated in models? These questions may be addressed under agreement RT 3.08, although that agreement specifically discusses fractured rock rather than alluvium.

#### **DOE Initial Response to GEN 1.01 (Comment 45)**

Flow transients are likely to occur, but it is unlikely that they will be as rapid or extreme as the transients associated with stopping and starting the pump at alluvial testing complex during single-well testing. However, it may be important to incorporate sudden transients associated with seismicity into models (it is well known that earthquakes can turn well water turbid for a while). Transients in water chemistry could also result in some remobilization of colloids. This issue is

related to KTI agreement RT 3.08 and will address both fractured rock and alluvium.

### **M.1.2 Related Key Technical Issues**

None.

## **M.2 RELEVANCE TO REPOSITORY PERFORMANCE**

The transport of colloids can influence the transport of radionuclides through the natural system. Therefore, this process is included in the transport model and is important in evaluating the saturated zone for the time scales of interest. Because natural colloids are omnipresent in the saturated zone and make it difficult to distinguish between natural and introduced colloids during field testing, Yucca Mountain Project scientists and other researchers have relied on the use of polystyrene microspheres as surrogates for natural colloids in field tracer tests (McKay et al. 2000; Auckenthaler et al. 2002; Harvey et al. 1989; Goldscheider et al. 2003; Becker et al. 1999; and Reimus and Haga 1999). Numerous laboratory studies involving microspheres as colloid analogs have also been conducted (Abdel-Fattah and El-Genk 1998; Anghel 2001; Reimus 2003; Vilks and Bachinski 1996; Toran and Palumbo 1992; McCaulou et al. 1995; Wan and Wilson 1994).

Even though they have different physical and chemical properties, the benefit of using microspheres as colloid tracers in these field tests overshadows the limitations because they can be obtained with a narrow range of diameters and with various fluorescent dyes incorporated into the polymer matrix, which allows them to be detected at low concentrations and to be discriminated from natural, nonfluorescing colloids. CML microspheres have been used in testing by the Yucca Mountain Project because these microspheres have more hydrophilic surfaces than other types of polystyrene microspheres. The hydrophilic surface is more representative of inorganic colloids, which also have hydrophilic surfaces.

Sections 3.2.1 and 3.3.2 contain summaries of how microsphere test results have been used to support Yucca Mountain performance assessments. Details of laboratory tests conducted to compare the transport behavior of microspheres and inorganic colloids in saturated fractured tuffs and saturated alluvium are provided in the *Saturated Zone Colloid Transport* report (BSC 2003, Section 6.8). These test results and their interpretation provide the basis for the DOE response to KTI RT 3.08.

## **M.3 RESPONSE**

### **M.3.1 Response to RT 3.08 AIN-1 Comment 1**

The NRC requested that the DOE provide a stronger technical basis and adequate experimental evidence to indicate that CML microspheres can be used as analogs for colloids in alluvium.

CML microspheres were used as surrogates for colloid tracers in the multiple-tracer tests in the Bullfrog Tuff and the Prow Pass Tuff at the C-Wells complex. CML microspheres were also used in one of the three single-well tracer tests in the saturated alluvium at borehole

NC-EWDP-19D1, and they will be used in at least one cross-hole tracer test at the Alluvial Testing Complex (ATC) (when permitting conditions allow further aquifer testing).

CML microspheres were selected as colloid tracers in these field tests because they are nearly monodisperse (i.e., they have a narrow range of diameters) and they can be obtained with various fluorescent dyes incorporated into the polymer matrix, which allows them to be detected at low concentrations and to be discriminated from natural, nonfluorescing colloids using methods such as epifluorescent microscopy and flow cytometry. Flow cytometry was used as the microsphere detection and quantification method for all field tracer tests in which microspheres were used as tracers. This technique allows quantification at microsphere concentrations as low as 100/mL in the presence of natural background colloid concentrations that are 2 to 4 orders of magnitude higher. These levels of detection and discrimination are not attainable using other types of colloid tracers, except perhaps viruses or bacteriophages (Bales et al. 1989, pp. 2063 to 2064).

Recent laboratory experiments (BSC 2003) conducted to evaluate the applicability of CML microspheres as field-test surrogates for inorganic colloids in saturated fractured media and saturated alluvium have demonstrated that CML microspheres can be used as conservative analogs in fractured tuffs and that small microspheres (less than 200 nm diameter) transport with nearly the same attenuation as natural colloids in alluvium. In laboratory fracture experiments, 330-nm-diameter CML microspheres consistently experienced less filtration and attenuation than 100-nm silica colloids. Additional tests showed that silica colloids transported with less attenuation than montmorillonite clay colloids. Furthermore, 640-nm-diameter microspheres transported with less attenuation in the C-wells Prow Pass Tuff field tracer test than 280-nm-diameter microspheres. The results suggest that microspheres in the 280- to 640-nm size range should transport conservatively relative to inorganic colloids. In alluvium-packed column experiments, natural colloids (wide range of diameters, most less than 100 nm) transported with slightly less filtration than 190-nm-diameter CML microspheres and with considerably less filtration than 500-nm microspheres. These results suggest that:

1. Small (less than 200-nm-diameter) CML microspheres should be reasonable surrogates for inorganic colloids in saturated alluvium.
2. CML microspheres in the 280- to 640-nm-diameter size range should be conservative colloid tracers in saturated fractured media (yielding transport parameter estimates that result in overprediction of inorganic colloid transport).

### **M.3.2 Response to RT 3.08 AIN-1 Comment 2**

The NRC requested that the DOE provide a response to GEN 1.01 (Comment 45) to address the potential for remobilization of microspheres and colloids.

The need for incorporating sudden transients into the transport models using features, events, and processes was evaluated. A response to the transient issue in the previous RT 3.08 submittal was not included because the DOE was in the process of developing a conceptualization of the appropriate models and had not yet decided on which transient processes (if any) would be important to incorporate in the models. Remobilization of colloids as a result of flow transients is not explicitly included in the process models carried forward to total system performance

assessment for the license application. However, parameter distributions developed for colloid retardation factors in the saturated zone will be partially based on detachment rates derived from field tests in which such flow transients occurred. These flow transients were the result of pumping interruptions and subsequent pumping resumption, so the transients were probably more severe than any likely to be encountered under ambient conditions. Thus, the effect of these transients on the retardation factor distributions is expected to be a reduction in the retardation factors such that the remobilization of colloids due to naturally occurring flow transients is effectively overestimated. Therefore, the explicit inclusion of minor transient colloid mobilization processes, as they apply to the overall total system performance assessment for license application modeling effort, is screened out.

The information in this report is responsive to agreements RT 3.08 AIN-1 and GEN 1.01 (Comments 43 and 45) made between the DOE and NRC. The report contains the information that DOE considers necessary for the NRC to review for closure of these agreements.

#### **M.4 BASIS FOR THE RESPONSE**

##### **M.4.1 Introduction to Microspheres as Analogs for Colloids**

Substantial additional laboratory analyses and interpretations have been completed since the original DOE submittal for RT 3.08 (Ziegler 2002; BSC 2003).

##### **M.4.2 Summary of Recent Laboratory Experiments Conducted for the U.S. Department of Energy**

Colloid filtration rate constants and retardation factors for the fractured volcanics have been estimated in a number of laboratory and field experiments conducted for the Yucca Mountain Project and the Underground Test Area Project. The field measurements in fractured tuffs involved fluorescent CML microspheres ranging in diameter from 280 to 640 nm. Microsphere analogs were used because testing with natural colloids is not practical in the saturated zone at Yucca Mountain where natural colloids are abundant, and it would not be possible to differentiate exogenous colloid breakthrough in tracer testing. CML polystyrene microspheres can be tagged with fluorescent dyes that allow them to be detected and quantified using specific wavelengths of light in recovered samples.

To evaluate potential differences in transport characteristics between the CML microspheres and natural colloids, additional laboratory analyses were conducted to reevaluate previous interpretations at Yucca Mountain and elsewhere in the DOE complex.

The process for determining colloid filtration and detachment rates,  $k_{filt}$  and  $k_{det}$ , respectively, from laboratory or field transport experiments is:

1. Nonsorbing solute tracers were always injected simultaneously with the colloid tracer(s). The mean residence time ( $L/V$ , where  $L$  is travel distance and  $V$  is velocity) and dispersivity ( $D/V$ , where  $D$  is the dispersion coefficient) in the flow system were determined using RELAP (LANL 2002) to fit the nonsorbing solute breakthrough curves. In dual-porosity systems, diffusive mass-transfer parameters were estimated for the solutes so that the effects of diffusion and dispersion could be distinguished in

the flow system. Diffusive mass-transfer parameters were determined by simultaneously fitting the responses of two nonsorbing tracers with different diffusion coefficients or fitting the responses of the same nonsorbing tracer at different flow rates through the systems. In field tests, because of the low tracer recovery in many cases, the fraction of tracer mass observed in the test was allowed to be an additional adjustable parameter for fitting the solute breakthrough curves. The best-fitting fraction for solutes was then applied to the colloids (although the colloids were assumed to not diffuse into the matrix) with the rationale that the flow pathways resulting in incomplete recovery of solutes would affect the simultaneously injected colloids similarly. This practice has been consistently followed in interpretations of microsphere and colloid transport tests, as colloid transport is generally reported relative to solute transport. The issue is not that colloids travel faster than solutes (in fact, this is not consistently observed unless travel times are extremely short, as in laboratory experiments) but that they can carry strongly-sorbing radionuclides along with them and they do not readily diffuse into the matrix, which makes their effective travel time shorter than solutes in systems with significant solute matrix diffusion. The latter difference between colloids and solutes is accounted for in the interpretive procedure. The velocity of colloids and solutes in fractures should be equal over long enough distances and times.

2. The mean residence time, dispersivity, and mass fraction (for field tests) obtained from fitting the solute breakthrough curves were assumed to apply to the colloids in each experiment.
3. RELAP was used to fit colloid breakthrough curves by adjusting  $k_{filt}$  and  $k_{det}$  (and fixing the mean residence time, dispersivity, and mass fraction to be equal to that of the solutes). The colloids are also assumed to not diffuse into the matrix. The procedure involved adjusting the colloid retardation factor,  $R_{col}$ , and  $k_{filt}$ . The relationship between  $R_{col}$ ,  $k_{filt}$ , and  $k_{det}$  is  $R_{col} = 1 + k_{filt}/k_{det}$ , so if  $R_{col}$  and  $k_{filt}$  are adjusted,  $k_{det}$  is adjusted by default.
4.  $R_{col}$  (and therefore,  $k_{det}$ ) was constrained primarily by fitting the tails of the colloid breakthrough curves.  $k_{filt}$  was constrained primarily by fitting the early (unretarded) colloid response (i.e., the peak arriving at about the same time as nonsorbing solutes). Essentially,  $k_{filt}$  was adjusted until it was small enough that the fraction of colloids not filtered in the system matched the early arriving peak. Therefore, the early colloid response was implicitly interpreted as being a fraction of colloids that moved through the system without filtering. Similarly,  $R_{col}$  was adjusted until an appropriate fraction of filtered colloids was predicted to detach, thereby yielding a modeled response that approximated the tails of the colloid breakthrough curves. For any given test, a single best-fitting  $k_{filt}$  is obtained. In most cases, this estimate is neither a lower nor an upper bound. A lower bound is obtained if there is no colloid breakthrough (which happened at least once). Attachment rates above this lower bound will also result in no colloid breakthrough. An upper bound is obtained if 100 percent of the colloids transport conservatively. Attachment rates below this upper bound will also result in 100 percent conservative transport.

In some tests, an inadvertent flow transient occurred that resulted in a “spike” in colloid concentrations in the tail of the breakthrough curve. This is presumably because of enhanced detachment caused by the flow transient. In these instances, the value obtained for  $R_{col}$  (and  $k_{det}$ ) was not considered to be representative of steady-flow conditions. However, the value obtained for  $k_{filt}$ , which was constrained primarily by the colloid response occurring before the flow transient, was assumed to be representative of steady-flow conditions. Thus,  $k_{filt}$  values obtained from such tests were used in the development of cumulative distribution functions for filtration rate constants, but  $R_{col}$  values from these tests were not used in the development of cumulative distribution functions for retardation factors.

#### **M.4.3 The Use of Polystyrene Microspheres as Tracer Surrogates for Inorganic Groundwater Colloids**

Many of the laboratory and field experiments used to develop the  $R_{col}$  distributions in this analysis used CML polystyrene microspheres to study colloid transport. This section describes the effectiveness of CML microspheres as analogs to inorganic groundwater colloids. CML microspheres were used as colloid tracers in the multiple-tracer tests in the Bullfrog Tuff and the Prow Pass Tuff at the C-Wells complex. CML microspheres were also used in a single-well tracer tests in the saturated alluvium at borehole NC-EWDP-19D1, and they will be used in at least one cross-hole tracer test at the ATC. CML microspheres were selected as colloid tracers in these field tests because they are nearly monodisperse, can be detected at very low concentrations, and can be discriminated from natural, nonfluorescing colloids using methods such as epifluorescent microscopy and flow cytometry. Flow cytometry has been used as the microsphere detection and quantification method for all field tracer tests in which microspheres have been used as tracers. This technique allows quantification at microsphere concentrations as low as 100/mL in the presence of natural background colloid concentrations that are 2 to 4 orders of magnitude higher. These levels of detection and discrimination are not attainable using other types of colloid tracers, except perhaps viruses or bacteriophages (Bales et al. 1989, pp. 2063 to 2064).

CML microspheres were chosen over other types of polystyrene latex microspheres as field colloid tracers for two reasons:

1. They have surface carboxyl groups that give them a negative surface charge at pH greater than about 5.
2. They have relatively hydrophilic surfaces compared to other types of polystyrene microspheres (Wan and Wilson 1994, Table 1).

These properties are consistent with those of natural inorganic groundwater colloids. In addition to providing better consistency with surface characteristics of inorganic colloids, these properties result in greater resistance to flocculation and less attachment to negatively charged hydrophilic rock surfaces. Fluorescent dyes are generally incorporated into the microspheres by swelling the spheres in an organic solvent containing the dye and then washing the spheres in an aqueous solution to expel the solvent and shrink them back to the original size. Dye molecules tend to remain in the spheres because of their affinity for the organic matrix. As discussed above, the dyes in the matrix provide the means for discriminating tracer colloids from natural colloids and for quantifying tracer colloid concentrations at low levels.

The CML microspheres used in Yucca Mountain field tracer tests were purchased from Interfacial Dynamics Corporation because they use a surfactant-free synthesis process that does not require microspheres to be cleaned (by dialysis or centrifugation) to remove trace levels of surfactant before they are used in tests. Small levels of surfactants can affect microsphere surface characteristics, resulting in inconsistency and irreproducibility of the transport behavior.

CML microspheres have properties that make them a suitable choice among synthetic polystyrene microspheres as reasonable surrogates for inorganic colloids. A comparison of properties of CML microspheres and naturally occurring inorganic groundwater colloids is presented in Table M-1. Although the two types of colloids differ in density, shape, and specific surface chemistry, both have negative surface charges (at groundwater pHs) and hydrophilic surfaces.

Table M-1. Comparison of Properties of CML Microspheres and Inorganic Groundwater Colloids

Property	CML Microspheres	Inorganic Groundwater Colloids
Size	Monodisperse but greater than 200 nm-diameter to ensure good fluorescence detection	Polydisperse, ranging from less than 50 nm to greater than 1000 nm (1 $\mu\text{m}$ )
Density	1.055 g/cm <sup>3</sup>	2.0 to 2.6 g/cm <sup>3</sup>
Shape	Spherical	Variable, including polygons, rods, and platelets
Surface Chemistry	Carboxyl groups with many polymer chains extending into solution	Variable, with silicate, iron oxide, aluminum oxide, manganese oxide, and other surface groups possible
Zeta potential	-30 mV or less in low ionic strength water at neutral pH	-30 mV or less in low ionic strength water at neutral pH
Hydrophobicity	Hydrophilic	Hydrophilic
pH at point of zero charge	About 5.0	Variable, but generally less 6

To address the suitability of using CML microspheres as surrogates for natural inorganic colloids, a limited number of laboratory experiments were conducted in which the transport behavior of CML microspheres was compared with that of silica microspheres in saturated volcanic-tuff fractures and saturated alluvium-packed columns. Tests were conducted using the same CML microspheres (330-nm-diameter spheres from Interfacial Dynamics Corporation dyed with a fluorescent yellow-green dye) and silica spheres (100-nm-diameter spheres from Nissan Chemical). Further information on the two colloid tracers is presented in Table M-2. Most of the tests involving the CML microspheres and silica colloids were conducted in vertically-oriented systems, but in one test in a horizontally-oriented fracture demonstrated that silica colloid transport was significantly more attenuated in this orientation than in the vertical orientation, presumably because of settling. The CML microspheres, on the other hand, were affected only slightly by the change from vertical to horizontal orientation. Silica microspheres were used in the comparison studies because previous testing indicated that silica microspheres transport with less attenuation through vertically oriented fractures than clay (montmorillonite) colloids (Kersting and Reimus 2003). Therefore, because CML microspheres transport with less attenuation than silica microspheres, they would also be expected to be transported with less attenuation than clay colloids.

The 330-nm CML microspheres were selected to be representative of microspheres with diameters ranging from about 250 to 500 nm, which represents a practical size range that can be used in field tests (detection-limited at the small end and cost-limited at the large end). Microspheres at the upper end of this size range will settle about twice as fast and diffuse about one-third slower than 330-nm-diameter spheres, and microspheres at the lower end of this range will settle about half as fast and diffuse about one-fourth faster than 330-nm-diameter spheres.

However, when comparing CML to silica, the CML microspheres ranging in size from 250 to 500 nm (diameter) will settle slower and diffuse slower than 100-nm silica microspheres. Both of these characteristics (slower settling and diffusion) are desirable for reducing the number of colloid collisions with aquifer surfaces. Thus, if electrostatic or double-layer interactions between colloids and aquifer surfaces are similar for both types of microspheres (as suggested by the similar zeta potentials; Table M-2), the CML microspheres would be expected to transport with less attenuation relative to the silica microspheres.

Testing in fractured volcanic rock was conducted in two different fractured cores from Pahute Mesa at the Nevada Test Site, with the majority of the testing being done in fractured lava. At the time of the testing, fractured cores from the saturated zone near Yucca Mountain were not readily available. Testing in the lava core was conducted at several flow rates and residence times.

Table M-2. Properties of CML and Silica Microspheres Used in Experiments

Property	CML Microspheres	Silica Microspheres
Particle Diameter (nm)	330 ± 11	100
% Solids (g/100g) <sup>a</sup>	2 ± 0.1	40.7
Stock Conc. (number/mL) <sup>a</sup>	1 x 10 <sup>12</sup>	3.8 x 10 <sup>14</sup>
Density (g/cm <sup>3</sup> )	1.055	2.65
Dye Excitation/Emission Wavelengths (nm)	505/515	No Dye
Diffusion Coefficient (cm <sup>2</sup> /s) <sup>b</sup>	1.34 x 10 <sup>-8</sup>	4.43 x 10 <sup>-8</sup>
Specific Surface Area (cm <sup>2</sup> /g)	1.7 x 10 <sup>5</sup>	2.3 x 10 <sup>5</sup>
Surface Charge (meq/g) <sup>c</sup>	0.08	not measured
Zeta Potential in U-20WW Water (mV) <sup>d</sup>	-42.7 ± 9.1	-41.2 ± 4.1
Zeta Potential in NC-EWDP-19D1 Water (mV)	NM	-45.15 ± 2.9

Source: Information from manufacturers' certificates of analyses or calculated as described in Note b below, except for zeta potentials. Zeta potentials are reported by Anghel (2001, Chapter 2).

- NOTES: <sup>a</sup> Manufacturer's stock solution in deionized water; solutions used in experiments were diluted in groundwater to several orders of magnitude below these concentrations.
- <sup>b</sup> Calculated using the Stokes-Einstein equation,  $D = kT/(6\pi\mu R)$ , where  $k$  = Boltzmann's constant ( $1.38 \times 10^{-16}$  ergs/K),  $T$  = temperature (K),  $\mu$  = fluid viscosity (g/cm-s), and  $R$  = colloid radius (cm). Calculations assume water at 25°C (298 K).
- <sup>c</sup> Value reported by the manufacturer (Interfacial Dynamics Corporation).
- <sup>d</sup> The zeta potential is the potential measured at the "surface of shear" near the colloid surface in solution (Hiemenz 1986, p. 745). The surface of shear occurs where ions transition from being immobile to being mobile relative to the colloid surface when the colloid moves relative to the surrounding solution. The zeta potential is generally considered to be the best experimental measure of the strength of electrostatic interactions between colloids or between colloids and surfaces in solution.

Conclusions from the testing suggest that CML microspheres in the size range of 280 to 640 nm in diameter should transport similarly to, or with less attenuation relative to, natural inorganic groundwater colloids in saturated fractured systems. However, in saturated alluvium systems, CML microspheres should be smaller than about 200-nm diameter to serve as reasonable analogs for inorganic colloids.

Two sets of experiments were conducted in which the transport of CML microspheres was compared to that of inorganic colloids in saturated alluvium. In the first set of experiments, 330-nm-diameter CML microspheres and 100-nm-diameter silica spheres were simultaneously injected into columns packed with alluvium from the uppermost-screened interval of borehole NC-EWDP-19D1. Water from the same interval was used in these experiments. In the second set of experiments, 190- and 500-nm-diameter CML microspheres were injected simultaneously with natural colloids collected from borehole NC-EWDP-19D1. The alluvium and water in these experiments were taken from the lowest screened interval completed in the alluvium at the ATC (the water came from borehole NC-EWDP-19D1, and the alluvium came from borehole NC-EWDP-19IM1A). In this set of experiments, Pu(V) was sorbed onto the natural colloids prior to injecting the colloids into the columns. Thus, these experiments also provided a test of colloid-facilitated plutonium transport in saturated alluvium, but the plutonium transport results are beyond the scope of this summary. Although the amount of colloid filtration was considerably different in the two sets of alluvium colloid-transport experiments, the results were consistent in that the inorganic colloids transported with similar or less filtration than the CML

microspheres in both sets of tests. However, it was also apparent in the second set of experiments that smaller CML microspheres tend to more closely approximate the transport behavior of natural inorganic colloids than larger microspheres in saturated alluvium. This result supports the hypothesis that interception may be a dominant mechanism of colloid filtration in alluvium because of the small pore throat sizes that are present. It also suggests that the smallest detectable CML microspheres should be used in field tracer tests in saturated alluvium to obtain field-scale colloid-transport parameters that are most representative of natural colloids.

#### **M.4.4 Ionic Strength**

Colloidal suspensions are sensitive to the ionic strength of the solution, and the results of previous investigations at the C-Wells complex and at Busted Butte suggest that the effects of ionic strength may have played important roles in those studies (DTN: GS011108312322.006). The original letter report (Ziegler 2002) did not discuss ionic strength of experimental fluids. Ionic strength effects should be explicitly considered in any studies involving transport of colloids or an explanation of why the exclusion of this effect would not have an adverse impact on performance should be documented.

It was an oversight to not include the ionic strengths of the groundwater used in the fractured core and alluvium column experiments involving CML microspheres and silica colloids. The ionic strengths were about 0.0035 M for the water used in the fractured core experiments (borehole U-20WW water) and about 0.004 M for the water used in the alluvium experiments (borehole NC-EWDP-19D water from Zones 1 and 2) (DTN: GS011108312322.006). Furthermore, the divalent cation concentrations (mostly  $\text{Ca}^{2+}$ ) in the two waters were low and almost identical (divalent cations have a greater destabilizing effect on colloids than monovalent cations). The solute tracers used in conjunction with the colloid tracers increased the ionic strength of the injection solutions by 0.001 to 0.0014 M in the experiments (up to a maximum of about 0.005 M) (DTN: GS011108312322.006).

These differences in solution ionic strength should not, by themselves, have been large enough to cause large differences in the transport behavior of the microspheres and silica colloids. It is expected that the silica colloids would be more sensitive to ionic strength than the CML microspheres because the microspheres have polymer strands extending from their surfaces that contribute to stability in aqueous solutions, whereas silica colloids are stabilized primarily by their negative surface charge. Thus, silica colloids would be expected to be more attenuated, instead of less attenuated, relative to CML microspheres in a higher ionic strength alluvium groundwater if all other things were equal. Therefore, CML microspheres are expected to be somewhat conservative.

Ionic strength was not varied in the experiments because the experimental objective was to compare the transport behavior of the colloid tracers in groundwaters considered to be representative of different saturated zone hydrogeologic settings. This study was limited in scope to saturated zone transport. Varying ionic strength would be more important in studies addressing transport in the unsaturated zone or in the engineered barrier system where greater potential variability in ionic strength could be expected.

In summary, while it has been shown that CML microspheres were good conservative analogs when used in the fractured tuffs at the C-Wells complex tracer studies, the recent laboratory investigations have revealed that some sizes of microspheres may not be conservative when used in alluvium. The testing suggests that small (less than 200-nm-diameter) CML microspheres should be reasonable surrogates for inorganic colloids in saturated alluvium. The single-well tracer testing did not yield usable results with microspheres. If testing of alluvium is resumed, the DOE will again evaluate all existing data, including any literature or studies done at other alluvium sites when developing a test plan. Scientists are also evaluating other methods of tagging natural colloids as a method to compare microsphere response with the response of modified introduced natural colloids. This response should provide the additional information requested as well as the technical basis for our response.

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#### **M.5.2 Data, Listed by Data Tracking Number**

GS011108312322.006. Field and Chemical Data Collected between 1/20/00 and 4/24/01 and Isotopic Data Collected between 12/11/98 and 11/6/00 from Wells in the Yucca Mountain Area, Nye County, Nevada. Submittal date: 11/20/2001.