

BSC

Model Administrative Change Notice

QA: QA
Page 1 of 5

Complete only applicable items.

1. Document Number:	MDL-NBS-HS-000008	2. Revision:	02	3. ACN:	01
4. Title:	Radionuclide Transport Models Under Ambient Conditions				
5. No. of Pages Attached	17				

6. Approvals:		
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7. Affected Pages	8. Description of Change:
x	<p>Corrected Table of Contents to reflect correct page numbering, change:</p> <p>9.1 DOCUMENTS CITED..... ERROR! BOOKMARK NOT DEFINED.</p> <p>To</p> <p>9.1 DOCUMENTS CITED..... 9-1</p> <p>This change was self-identified</p>

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6-24	<p>Revised Text for clarification</p> <p>Section 6.1.5.2 “Stipulations/Approaches/Simplifications Involved in Transport Processes”, #9, Justification, change:</p> <p><i>Justification: Ambient tracers and radionuclides escaping from the repository are expected to occur at concentrations that are too low to affect the aqueous solution density (BSC 2004 [DIRS 169856], Section 6).</i></p> <p>To</p> <p><i>The release of radionuclides and other dissolved substances into water exiting the drifts increases both the density and dynamic viscosity. Gravity-driven flow is inversely proportional to the kinematic viscosity (dynamic viscosity divided by density), while purely pressure-driven flow is inversely proportional to the dynamic viscosity (BSC 2004 [DIRS 169861], Section E1). In general the dynamic viscosity increases with concentration faster than the density, so that kinematic viscosity increases with concentration. The relative change in either the kinematic or dynamic viscosity resulting from increased concentration is generally bounded by a factor of two. (Kestin et al. 1981 [DIRS 173192]; Kestin et al. 1981 [DIRS 173191]; Qadeer 2004 [DIRS 173190], Tables 1 and 3). Increased viscosity resulting from increased concentration would reduce the flow rate. Therefore, these effects are expected to be negligible or result in reduced rates of flow carrying radionuclides. These effects are generally small compared to other uncertainties in the flow rate which range over more than an order of magnitude (BSC 2004 [DIRS 169861], Table 6.1-2).</i></p> <p>The need for this clarification was self-identified</p>				
9-11	<p>Citation update (Correct DIRS as appropriate)</p> <p>Section 9.1 “DOCUMENTS CITED”, add reference [DIRS 173192], add to read:</p> <p><i>Kestin, J.; Khalifa, H.E.; and Correia, R.J. 1981. “Tables of the Dynamic and Kinematic Viscosity of Aqueous KCl Solutions in the Temperature Range 25-150 °C and the Pressure Range 0.1-35 MPa.” Journal of Physical and Chemical Reference Data, 10, (1), 57-70. Washington, D.C.: American Chemical Society, American Institute of Physics. TIC: 257104.</i></p> <p>This change was self-identified</p>				

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9-11	<p>Citation update (Correct DIRS as appropriate)</p> <p>Section 9.1 "DOCUMENTS CITED", add reference [DIRS 173191], add to read:</p> <p><i>Kestin, J.; Khalifa, H.E.; and Correia, R.J. 1981. "Tables of the Dynamic and Kinematic Viscosity of Aqueous NaCl Solutions in the Temperature Range 20-150 °C and the Pressure Range 0.1-35 MPa." Journal of Physical and Chemical Reference Data, 10, (1), 71-87. Washington, D.C.: American Chemical Society, American Institute of Physics. TIC: 257105.</i></p> <p>This change was self-identified</p>				
9-15	<p>Citation update (Correct DIRS as appropriate)</p> <p>Section 9.1 "DOCUMENTS CITED", add reference [DIRS 173190], add to read:</p> <p><i>Qadeer, R. 2004. "Concentration and Temperature Dependence of Viscosity of Uranium Solutions in H₂O and 3mol/L HNO₃." Journal of Zhejiang University Science, 5, (4), 457-461. Hangzhou, P.R., China: Zhejiang University Press. TIC: 257142.</i></p> <p>This change was self-identified</p>				
A-5	<p>Citation update</p> <p>Section A4 "Water Compositional Ranges Along Transport Pathways", 2nd line, change:</p> <p><i>Analysis of Geochemical Data for the Unsaturated Zone (BSC 2004 [DIRS 169734], Section 5.2.2.4).</i> To <i>Yucca Mountain Site Description (BSC 2004 [DIRS 169734], Section 5.2.2.4)</i></p> <p>This change was self-identified</p>				
A-7	<p>Typographical error</p> <p>Section A6 "Approach to the Derivation of Kd Ranges for Major Rock Types in the Yucca Mountain Flow System", 3rd paragraph, line 4, remove solidus (forward slash), change:</p> <p><i>".....model to evaluate /the impact of variations....."</i> To <i>".....model to evaluate the impact of variations....."</i></p> <p>This change was self-identified</p>				

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A-9	<p>Added text for clarification</p> <p>Section A8 “Discussion and Analysis of Experimental Sorption Coefficient Data and Surface Complexation Modeling”, add to the end of the paragraph:</p> <p><i>“Points to plot a cumulative distribution function (cdf) of K_d values were calculated by ranking n relevant K_d values, and assigning the cdf value (i/n) to the i^{th} point”.</i></p> <p>The need for this clarification was self-identified</p>				
A-9	<p>Typographical error</p> <p>Section A8.1 “Americium”, 3rd paragraph, line 3, last word, change:</p> <p><i>lead</i> To <i>led</i></p> <p>This change was self-identified</p>				
A-73	<p>Change to figure</p> <p>Figure A-59b “Empirical Cumulative Distribution for Strontium Sorption Coefficients on Devitrified Tuff”, <i>add one point for devitrified tuff.</i></p> <p>Note: This figure is used for illustration only. The change does not affect the product output</p> <p>This error was identified in CR 5732</p>				
A-73	<p>Citation update</p> <p>Figure A-59b “Empirical Cumulative Distribution for Strontium Sorption Coefficients on Devitrified Tuff”, change the description for this figure to read:</p> <p><i>“Empirical Cumulative Distribution for Thorium Sorption Coefficients on Devitrified Tuff”</i></p> <p>This error was identified in CR 5200</p>				

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4. Title:	Radionuclide Transport Models Under Ambient Conditions				
A-74	<p>Citation update</p> <p>Figure A-59c “Empirical Cumulative Distribution for Strontium Sorption Coefficients on Zeolitic Tuff”, change the description for this figure to read:</p> <p><i>“Empirical Cumulative Distribution for Thorium Sorption Coefficients on Zeolitic Tuff”</i></p> <p>This error was identified in CR 5200</p>				
A-74	<p>Change to figure</p> <p>Figure A-59d “Empirical Cumulative Distribution for Strontium Sorption Coefficients on Vitric Tuff”. In the “old” version, one point that had data for devitrified tuff was mistakenly classified as vitric tuff. <i>Delete one point which is not vitric tuff.</i></p> <p>Note: This figure is used for illustration only. The change does not affect the product output</p> <p>This error was identified in CR 5732</p>				
A-74	<p>Citation update</p> <p>Figure A-59d “Empirical Cumulative Distribution for Strontium Sorption Coefficients on Vitric Tuff”, change the description for this figure to read:</p> <p><i>“Empirical Cumulative Distribution for Thorium Sorption Coefficients on Vitric Tuff”</i></p> <p>This error was identified in CR 5200</p>				
I-1 through I-5	<p>Typographical error</p> <p>Footnote on pages I-1 through I-5, change:</p> <p>MDL-NBS-HS-000008 REV</p> <p>To</p> <p><i>MDL-NBS-HS-000008 REV 02</i></p> <p>This change was self-identified</p>				

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temperature increases over the ambient are expected after radioactive waste emplacement in the repository (BSC 2004 [DIRS 169856], Section 6).

An increasing temperature leads to a higher D_0 value according to the relationship discussed in Section 6.1.2.9 of this model report. Based on this relationship, an increase in temperature from 20°C (at the top of the UZ domain) to 30°C (at the water table, i.e., the bottom of the UZ domain) leads to an increase of D_0 by about 30 percent.

The effect of temperature on sorption is less well-defined. However, as is explained in Appendix I, corrections for temperature effects would be small and differences in physico-chemical conditions between laboratory and the field would likely introduce uncertainties larger than corrections for temperature.

Colloid filtration (deposition) generally follows a kinetic process (see Sections 6.2.3 and 6.18.2 in this model report). Equation 6-31 in this model report indicates that an increase in temperature increases the forward filtration coefficient κ^+ , indicating an increase in the filtration (deposition, clogging) rate. There is no information on the effect of temperature on the reverse filtration coefficient κ^- .

Thus, an increasing temperature in the UZ enhances diffusion (a particularly important mechanism in species mass transfer from the flow-dominating fractures to the matrix) and increases sorption and/or filtration. The cumulative effect is slower transport. The assumption of isothermal transport should not be viewed as an approximation of the prevailing conditions in the UZ, but rather as a condition that reflects a worst-case transport scenario and leads to conservative estimates of radionuclide transport times to the water table. Investigation of the effect of water-phase changes on transport may be included in future revisions of the present model report.

Applicability: This simplification is used in all studies in this model report (Sections 6.8 to 6.20, Section 7). No further confirmation is required for the purposes of this study.

9. The concentration of the radioactive solutes or colloids is at a tracer level, that is, too low to have any measurable effect on the flow regime.

Justification: The release of radionuclides and other dissolved substances into water exiting the drifts increases both the density and dynamic viscosity. Gravity-driven flow is inversely proportional to the kinematic viscosity (dynamic viscosity divided by density), while purely pressure-driven flow is inversely proportional to the dynamic viscosity (BSC 2004 [DIRS 169861], Section E1). In general the dynamic viscosity increases with concentration faster than the density, so that kinematic viscosity increases with concentration. The relative change in either the kinematic or dynamic viscosity resulting from increased

concentration is generally bounded by a factor of two. (Kestin et al. 1981 [DIRS 173192]; Kestin et al. 1981 [DIRS 173191]; Qadeer 2004 [DIRS 173190], Tables 1 and 3). Increased viscosity resulting from increased concentration would reduce the flow rate. Therefore, these effects are expected to be negligible or result in reduced rates of flow carrying radionuclides. These effects are generally small compared to other uncertainties in the flow rate which range over more than an order of magnitude (BSC 2004 [DIRS 169861], Table 6.1-2).

Applicability: This approximation is used in all studies in this model report (Sections 6.8 to 6.20 and Section 7). No further confirmation is required for the purposes of this study.

10. There is no phase change, that is, no water evaporation and condensation.

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- Kestin, J.; Khalifa, H.E.; and Correia, R.J. 1981. "Tables of the Dynamic and Kinematic Viscosity of Aqueous NaCl Solutions in the Temperature Range 20-150°C and the Pressure Range 0.1-35 MPa." *Journal of Physical and Chemical Reference Data*, 10, (1), 71-87. Washington, D.C.: American Chemical Society, American Institute of Physics. TIC: 257105. 173191
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Sorption coefficients for the radionuclides of interest can be a function of the concentrations of the radionuclides present in solution. Thus, experiments have been carried out as a function of radionuclide concentrations for most of the elements of interest. In most cases, experiments were carried out over a range of concentrations up to a solubility limit. Above the solubility limit, a solid phase incorporating the element of interest is precipitated out of solution. Therefore, the concentration of an element in solution cannot rise much higher than the solubility limit. Experiments in which the final solution concentrations for a given element of interest exceeded the solubility limit are not useful in this analysis and will be rejected.

Because experiments have been carried out at concentrations up to the solubility limit for most elements of interest, the experimental results and the probability distributions derived from them include this dependency. The only element for which the experimental concentrations did not approach a solubility limit was Cs. The solubility of cesium compounds is very high in Yucca Mountain waters (BSC 2004 [DIRS 169425], Section 6.17). Thus, the sorption coefficient probability distributions for cesium must be calibrated to the Cs concentrations expected in the UZ.

A4. WATER COMPOSITIONAL RANGES ALONG TRANSPORT PATHWAYS

The chemistry of pore waters and perched waters in the UZ along potential flow paths to the accessible environment is discussed in the *Yucca Mountain Site Description* (BSC 2004 [DIRS 169734], Section 5.2.2.4). In the UZ, two rather distinct water types exist in the ambient system. One is perched water and the other is pore water. Perched water is generally more dilute than pore water.

Table A-2. Composition of Yucca Mountain UZ Waters

Element	Units	J-13 ^a	Range of concentrations in perched waters ^b	Range of concentrations in pore waters within and below repository horizon ^c	UE 25 p#1-c Carbonate aquifer ^a	Synthetic p#1
Ca	mg/L	11.5	2.9–45	0.3–91.8	87.8	
Mg	mg/L	1.76	0–4.1	0–24.6	31.9	
Na	mg/L	45	34–98	3–207	171	261
K	mg/L	5.3	3.6–5.8	1.4–148.7	13.4	
SiO ₂	mg/L	64.2	7.7–64	5–352	64.2	
Cl	mg/L	6.4	4.1–16	6–130	37	
SO ₄	mg/L	18.1	4–223	6–101.1	129	
HCO ₃	mg/L	128	112–197	8–384	666	691
pH		6.9	7.6–8.7	6.7–9.7	6.7	

^a DTN: Ogard and Kerrisk (1984 [DIRS 100783], Table 1).

^b DTN: GS951208312272.004 [DIRS 165858].

^c DTN: GS010708312272.002 [DIRS 156375]; GS011008312272.004 [DIRS 165859]; GS990208312272.001 [DIRS 146134]; GS010608312272.001 [DIRS 165860]; GS000608312271.001 [DIRS 153407].

One gram of crushed rock material was added to a test tube with 20 mL groundwater spiked with the radionuclide(s) of interest. The test tube was put on a shaker table for a predetermined period to allow reaction to occur. After the predetermined time had passed, the solution was separated from the solid phase by either centrifugation or filtration. Centrifugation was preferred for those elements thought to have an affinity for the filter medium. The separations were not always perfect, due to various experimental constraints. In some cases, the solid fraction was separately counted. A sorption coefficient was usually calculated from the difference between the initial and final solution concentrations. Corrections were generally made for sorption onto the surface of the test tube during the equilibration (shaking) period.

Some potential sources of errors and experimental artifacts that may pertain to the sorption coefficients obtained at Los Alamos include weighing errors, counting errors, errors resulting from solutions being oversaturated with the element of interest, errors from imperfect solid/liquid separations, errors from inaccurate correction for sorption onto container walls, recording errors, transcription errors, inadvertent laboratory errors, and calculation errors. These errors cannot be quantitatively assessed. However, their existence will become apparent in the scatter of the data on diagrams presented in a later section.

A6. APPROACH TO THE DERIVATION OF K_D RANGES FOR MAJOR ROCK TYPES IN THE YUCCA MOUNTAIN FLOW SYSTEM.

The derivation of sorption coefficient probability distributions for the elements of interest on the major rock types in Yucca Mountain involves both an evaluation of available experimental data and sorption modeling. Experimental data will be used to evaluate the impact of variations in rock sorption properties within each of the rock types, radionuclide concentrations, sorption kinetics, and water chemistry on sorption coefficients for the elements of interest.

The radionuclides of interest are divided into three groups of radioelements. For the first group, including Am, Np, Pa, Pu, Th, and U, experimental data is used to evaluate the impact of radionuclide concentrations, sorption kinetics, and variations in water chemistry on sorption coefficients. Surface complexation modeling is used to further evaluate the impact of variations in water chemistry and surface area on sorption coefficients. The surface complexation models used in this analysis are based on the software code PHREEQC V2.3. The binding constants required for surface complexation modeling are either obtained from the literature or derived from experimental data involving sorption of the radioelement on quartz (see discussion in Section A7).

In the second group of elements, including Cs, Pa, Ra, and Sr, the ranges of sorption coefficient values for the major rock types are derived directly from the available experimental data and the ranges for environmental variables expected in the transport system. Although it would be preferable to have a theoretical model to evaluate the impact of variations in water chemistry and rock chemistry on sorption coefficients for these radionuclides, sufficient data are not available to properly constrain such a model.

For the third group, including carbon, iodine, and technetium, the sorption coefficient is set to zero in volcanic rocks and in alluvium.

sodium on silica (the same value was used for potassium). The total site concentrations were obtained from surface areas reported in *Batch Sorption Results for Neptunium Transport Through Yucca Mountain Tuffs* (Triay et al. 1996 [DIRS 101023], p. 62) and a site density of 2.3 sites/nm² as recommended by Pabalan et al. (1998 [DIRS 162987], p. 124). The thermo-dynamic database used for the modeling was the LLNL.DAT database supplied with the baselined YMP version of the PHREEQC V2.3 code.

A8. DISCUSSION AND ANALYSIS OF EXPERIMENTAL SORPTION COEFFICIENT DATA AND SURFACE COMPLEXATION MODELING

The data and modeling results for each element are discussed in separate sections. The sections are arranged in alphabetical order. Points to plot a cumulative distribution function (cdf) of K_d values were calculated by ranking n relevant K_d values, and assigning the cdf value (i/n) to the i^{th} point.

A8.1. AMERICIUM

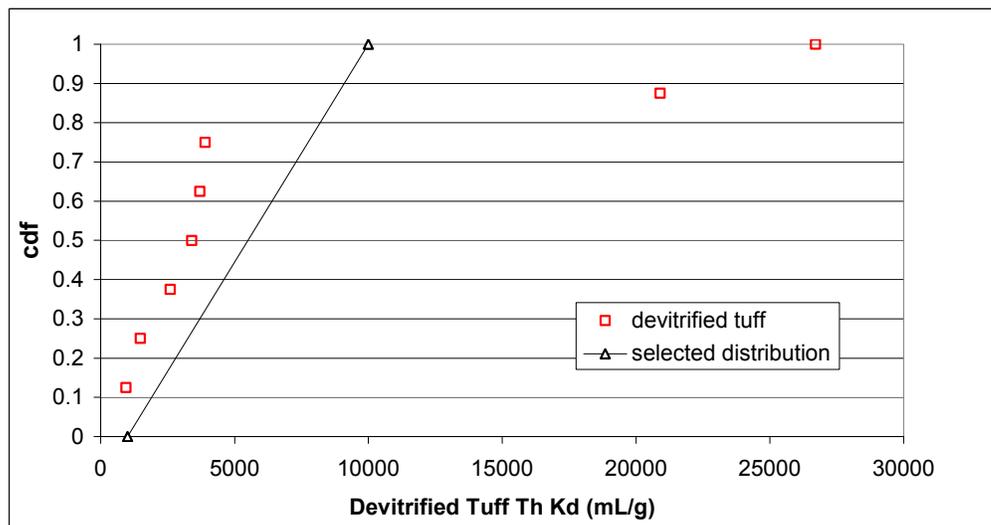
According to Nitsche et al. (1993 [DIRS 155218], pp. 78, 86), the solubility of americium in J-13 water is controlled by $\text{Am}(\text{OH})\text{CO}_3$. At pH = 8.5, the solubility is $2.4 (+/-1.9) \times 10^{-9}$ moles/Liter at 25°C. At pH = 7.0, the solubility is $1.2 (+/-0.3) \times 10^{-9}$ moles/Liter at 25°C. No Am sorption experiments were conducted in the UE 25 p#1-c water or in the synthetic p#1 water.

The differences in the Am solubility values reported in *Measured Solubilities and Speciations of Neptunium, Plutonium, and Americium in a Typical Groundwater (J-13) from the Yucca Mountain Region* (Nitsche et al. 1993 [155218]) and in the report *Dissolved Concentration Limits of Radioactive Elements* (BSC 2004 [DIRS 169425], Section 6.9) could reflect the impact of coprecipitation reactions on the Nitsche et al. (1993) experiments. As noted by Nitsche et al. (1993 [DIRS 155218]), Am behaves very similarly to the lanthanide element neodymium. Neodymium is a member of the lanthanide series elements. The elements of this series behave similarly in chemical reactions. The lanthanide series (also called the rare earth elements) includes La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb. The chemistry of the element Y is very similar to the chemistry of the lanthanide series elements and is usually included in discussion of the series.

The experiments reported in Nitsche et al. (1993 [155218]) were carried out using natural J-13 water. This water would have contained some concentration of each of the lanthanide series elements and Y. The presence of a rare earth element (REE) and Y in this water could have led to the coprecipitation of Am with REE and Y in a solid solution (i.e., Am-REE-YOHCO_3) during the experiments carried out by Nitsche et al (1993). This solid solution would have precipitated at lower Am concentrations than would have been the case if the REE and Y had not been present in J-13 water. In effect, some significant fraction of the concentrations of the REE and Y would be added to the concentration of Am in the solubility product.

The solubility calculations carried out in the BSC report (BSC 2004 [DIRS 169425], Section 6.9) did not consider the effects of trace elements, in particular the rare earth elements and Y. This

may explain the differences in the solubility values obtained experimentally (Nitsche et al. 1993 [DIRS 155218]) and theoretically (BSC 2004 [DIRS 169425], Section 6.9).



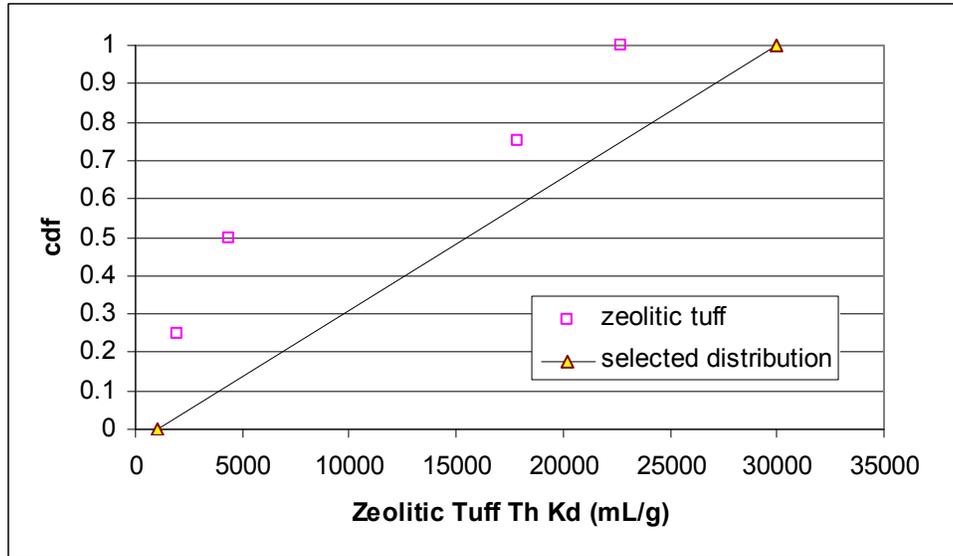
DTN: LA0305AM831341.001 [DIRS 163789].

Figure A-59b. Empirical Cumulative Distribution for Thorium Sorption Coefficients on Devitrified Tuff

A8.8.3 Vitric Tuff

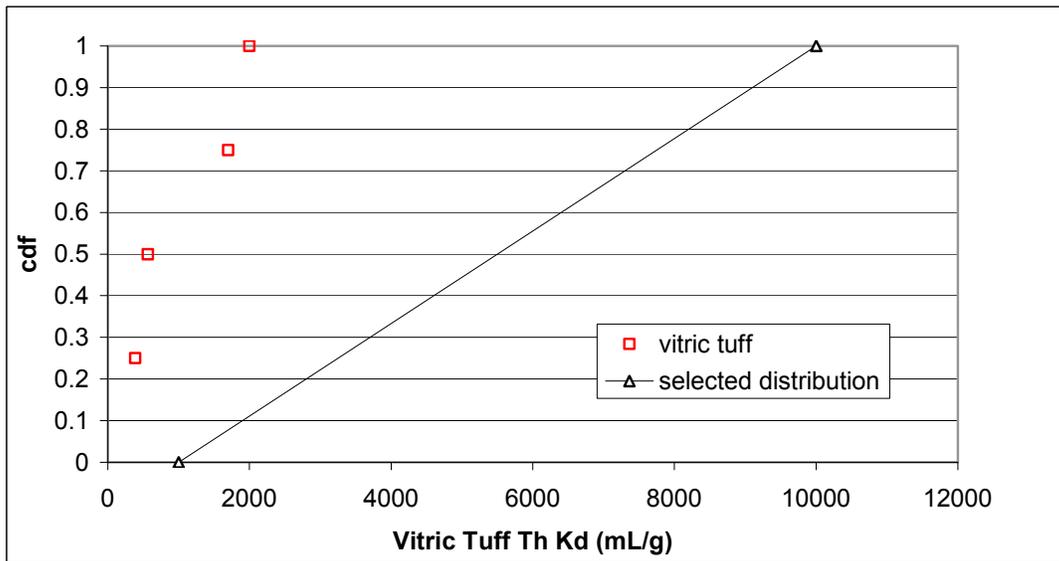
Sorption coefficient data for vitric tuff are plotted in Figures A-58 and A-59a. Based on the available data, vitric tuffs have sorption coefficients for thorium in the range of those obtained for the other tuffs in those experiments that were undersaturated in thorium dioxide.

Based on the data plotted in Figures A-58 and A-59a, the range of thorium sorption coefficients selected for vitric tuffs in the unsaturated volcanic section at Yucca Mountain is 1,000 to 10,000 mL/g. A uniform distribution is selected for vitric tuffs. Figure A-59d shows the empirical cumulative distribution for all the measured thorium sorption coefficients on vitric tuff in the UZ with the selected distribution superimposed. As discussed in Section A6., not all the empirical data was equally weighted in selecting the probability distribution as the influence of expected variations in water chemistry, radionuclide concentrations, and variations in rock surface properties within each major rock type were incorporated in making the selection.



DTN: LA0305AM831341.001 [DIRS 163789].

Figure A-59c. Empirical Cumulative Distribution for Thorium Sorption Coefficients on Zeolitic Tuff



DTN: LA0305AM831341.001 [DIRS 163789].

Figure A-59d. Empirical Cumulative Distribution for Thorium Sorption Coefficients on Vitric Tuff

II. TEMPERATURE EFFECT ON RADIONUCLIDE SORPTION

Potential variations with temperature in the value of the sorption (distribution) coefficient, K_d , for a given radionuclide with respect to a host rock substrate could be important when modeling radionuclide transport in the near field of the nuclear waste repository at Yucca Mountain, Nevada. The near field is considered that region around the repository subject to temperature perturbations caused by radioactive decay of the waste. At Yucca Mountain, radionuclide transport in the unsaturated zone is restricted above about 95° C by the absence of a mobile liquid aqueous phase. Therefore, the temperature range of interest would normally range between approximately 0 and 100° C. Another potential reason for understanding variations in K_d with temperature would be the need for making precise corrections in K_d for temperature differences between laboratory experimental conditions and ambient conditions in the far field. However, as examined further below, such corrections would be small, and in any case, differences in physico-chemical conditions between laboratory and the field would probably introduce uncertainties larger than corrections for temperature.

II.1 CONCEPTUAL MODEL

Radionuclide sorption involves the uptake of ionic or molecular species of that radionuclide (associated in most cases with nonradioactive isotopes of the same element) from an aqueous solution onto a solid phase. Sorption, R_s , is usually presented as the ratio of the radionuclide partitioned between the aqueous and solid phases, expressed as the percentage sorbed, thus,

$$R_s = 100(A_i - A_f)/A_f \quad (\text{Eq. I-1})$$

where A is measured in disintegration counts/second or Bq, and the subscripts, i and f , refer to the initial and final concentrations, respectively. Because a given concentration of a radioelement in solution is normally spiked with a known activity of one of its corresponding radionuclides, the final concentration of the radioelement in solution can easily be calculated. Thus, $A_i \propto C_o$, where C_o is the initial concentration, usually given as the molarity, mol/mL, and $A_i - A_f \propto (C_o - C_f)$, equivalent to the moles sorbed on a given mass of solid. The ratio is then expressed as:

$$R_d = (C_o - C_f)/C_f \cdot V/m \text{ (mL/g)} \quad (\text{Eq. I-2})$$

where V is the volume of solution in mL, and m is the mass of sorbent in g. Use of the term R_d implies that thermodynamic equilibrium has not necessarily been achieved. Upon achievement of equilibrium, R_d can be equated with K_d , the sorption (or distribution) coefficient, which is also expressed in units of mL/g.

If measurements to determine K_d are made at different temperatures, then the dependence of K_d on temperature can be evaluated. This dependence has a thermodynamic basis, which is defined further under Section II.3.2.

Simple models incorporating the K_d term have the advantage of economical data acquisition and convenient incorporation in hydrological computer codes. However, their ability to replicate radionuclide transport in the near field of a nuclear waste repository is less than optimal. Experience with the environmental remediation of contaminated aquifers has demonstrated that

transport models incorporating K_d seriously underestimate the length of time required for cleanup and grossly overestimate the maximum concentration at the time of breakthrough when compared with a model incorporating site complexation (Bethke and Brady 2000 [DIRS 154437]). However, the objective of aquifer remediation is opposite to that of using a geologic formation as a natural barrier to radionuclide migration. In the former, the goal is to lower groundwater contamination permanently to some mandated standard acceptable for drinking water, whereas in the latter, the goal is to ensure that the radionuclide activity penetrating the geologic barrier never rises above specified limits. The use of K_d formulations to predict radionuclide transport is therefore inherently conservative, because it tends to over-predict the maximum concentration in solution upon breakthrough to the so-called “accessible environment” when compared with site complexation models for a given set of conditions. Thus, such modeling would be consistent with regulatory guidelines requiring conservatism in predicting radionuclide release, that is, at earlier times and at higher concentrations than would be predicted using more sophisticated site complexation models as illustrated by Bethke and Brady (2000 [DIRS 154437]).

In the following analysis, the temperature dependence of radionuclide sorption is based on an evaluation of empirically determined K_d values at discrete temperatures. This approach is taken for the following technical and pragmatic reasons:

- The application of a simple linear isotherm for a given radionuclide, that is, experimentally determined K_d value, in computing radionuclide transport is inherently conservative in relation to more sophisticated site complexation models, because the breakthrough concentration to the accessible environment for a given set of conditions is over-predicted. Therefore, if an analysis using K_d s demonstrates acceptable confinement of radionuclides by the repository natural barriers, the use of linear isotherms can be justified as being adequate for their intended purpose.
- An initial examination of the available qualified (and unqualified) data pertaining to the sorption of radionuclides on tuff samples from Yucca Mountain and used in the following analysis did not indicate *a priori* that the data were of sufficient quality or sufficiently detailed to permit their use in more sophisticated models. The primary reason is that the temperature intervals at which K_d measurements were made are insufficient in number, and too widely spaced over the temperature interval of interest to permit identification of possible changes in the enthalpy of sorption with temperature (reflecting changes in sorption mechanism). Furthermore, unequivocal evidence of sorption reaction reversibility, necessary for any analysis where an equilibrium state is assumed, was not clearly demonstrated.
- Time constraints were such that no more than an exploratory evaluation could be conducted in which the adequacy and limitations of the temperature dependence of the linear isotherm could be assessed for those radionuclides for which data were available.
- Section 5 of this report assumes the validity of the linear isotherm for modeling radionuclide transport in matrix and fractures of the unsaturated zone at Yucca Mountain. The evaluation conducted in this appendix is, therefore, consistent with that assumption in Section 5 of this report.

II.2 ALTERNATIVE CONCEPTUAL MODELS

Models describing sorption range from the most primitive, for example that represented by the K_d term discussed above, to complex multisite surface complexation models. The choice of model for a particular application depends on the nature of the application and the degree of accuracy required. In the following paragraphs, some alternative models are briefly described that could be used, with potential improvements in the accuracy of predictive radionuclide transport simulations.

In Section II.1, it is implicitly assumed that a single K_d value is constant for all radioelement concentrations at a given temperature. This assumption is based on an analysis of an isothermal series of measurements with differing initial aqueous concentrations of a given sorbent, sometimes over many decades of concentration. The resulting logarithms of the sorbed concentration can be plotted in relation to the corresponding logarithms of the equilibrium concentration in solution. Various equations expressing this relationship have been developed, and are referred to as isotherms. The most commonly assumed relationship is the linear isotherm:

$$\text{Log } C_e = \text{Log } Q + k \quad (\text{Eq. I-3})$$

where C_e is the equilibrium concentration of the sorbent in mol/L, usually equivalent to C_f , and Q is the amount adsorbed in mol/g. Rearranging Equation I-3 yields $\text{Log } (C_e/Q) = k$ and $k = \log K_d$. This relationship is the basis for applications using K_d values in determinations of radionuclide transport at Yucca Mountain, as discussed above. In practice, experimentally determined isotherms are better fitted to more complex terms, the most common being the Freundlich isotherm (Freundlich 1926 [DIRS 165848]):

$$\text{Log } C_e = n \text{Log } Q + k \quad (\text{Eq. I-4})$$

where n and k are fitting parameters, and the Langmuir isotherm is (Langmuir 1918 [DIRS 126305]):

$$C_e/Q = 1/(BC_m) + (1/C_m) \cdot C_e \quad (\text{Eq. I-5})$$

where C_m is the sorption capacity in mol/g, and B is a constant related to the heat of sorption. The applicability of each isotherm varies with the nature of the sorption process under investigation. It can be associated with specific sorption mechanisms, although model fitting is usually empirical. The nature of the sorption process, whether chemical or physical adsorption, ion exchange, or even precipitation, is commonly ignored. Thus, the term “sorption” is used in this model report rather than adsorption, unless the process has been specifically identified as the latter. The Freundlich isotherm, in particular, has enjoyed a large measure of success in fitting sorption data, and was long thought to have no theoretical basis. However, Sposito (1980 [DIRS 127235]) determined that the Freundlich isotherm reflects the competitive adsorption of a tracer species in the presence of another species at much higher concentration. The theoretical basis for the Langmuir isotherm involves adsorption of a sorbent monolayer.

Other isotherms also have been formulated, particularly in relation to separation technology, such as the adsorption of gaseous and aqueous organic and inorganic species on activated carbon, or the adsorption of fatty acids on mineral surfaces for the purpose of selective flotation. These isotherms, such as the Flory-Huggins, Frumkin, and Dubinin-Radushkevich (D-R) equations (Yehia et al. 1993 [DIRS 164922]; Atun et al. 1996 [DIRS 164865]; Sabah et al. 2002 [DIRS 164909]; Kara et al. 2003 [DIRS 164880]) could be potentially useful in describing radioelement adsorption on Yucca Mountain host rock minerals. Evaluation as to their suitability for that purpose is, however, beyond the scope of this model report. Finally, it should be noted that composite sorption models, invoking additive combinations of various sorption isotherms to describe sorption behavior, have been applied to describe adequately some experimental data (e.g., see Weber et al. 1992 [DIRS 165228]).

The applicability of various isotherms is restricted to the experimental conditions under which they are tested. Models that permit predictions of sorptive behavior over a range of conditions, taking into account the effect of varying pH, competition between aqueous species, variations in ionic strength, and multiple adsorption sites, require much more sophisticated models. To address this problem, a variety of surface complexation models have been developed. These models require the precise measurement of more parameters and a more rigorous definition of the conditions to be modeled than isotherm models. The basis for these models is recognition that mineral surfaces are invariably electrically charged, the charge arising from unsatisfied valences caused by the discontinuity in a crystal structure, or from polarization of molecules or atoms at the interface. Minerals in sediments and soils are usually negatively charged. The charge, which is intrinsic to the mineral, is referred to as a permanent structural charge. In the aqueous phase, this charge is partially satisfied by a tightly coordinated layer of so-called potential determining ions, which bind to the exposed functional groups on the mineral. The surface charge resulting from this coordinated layer of ions may be either negative or positive. To preserve electrical neutrality, a diffuse layer of counter-ions must accumulate in the aqueous phase adjacent to the surface. The resulting interfacial structure containing the surface layer with its attendant tightly coordinated ions and the diffuse layer of counter-ions is referred to as the electrical double layer (EDL). The thickness of the EDL varies with ionic strength of the aqueous phase. The distribution of ionic species in the coordinated and diffuse layers is some function of the surface properties of the mineral and the activities of competing solutes in the aqueous phase.

To predict quantitatively the adsorption of a given solute, an electrostatic model is required that reproduces the behavior of the electrical double layer in relation to the solute species. The history of the development of surface complexation models incorporating the EDL spans a period of more than 80 years. Bolt (1991 [DIRS 165056]), Bolt and Van Riemsdijk (1991 [DIRS 165188]), Sposito (1984 [DIRS 127253]), Westall (1987 [DIRS 127323]), and Davis and Kent (1990 [DIRS 143280]) give historical reviews. Presently, three such surface complexation models have found widespread use, and are referred to respectively as the “constant capacitance,” “double layer,” and “triple layer” models. Detailed discussion of their formulation and theoretical basis can be found in the above-cited references.

Despite the promise of such models in predicting the adsorption behavior of aqueous species on mineral surfaces, they have serious limitations. The large majority of studies to quantify the surface complexation constants of aqueous species have been conducted on a limited set of

substrates, such as “hydrous ferric oxide,” α -alumina, aluminum hydroxide (usually gibbsite), and amorphous silica. Studies involving minerals of relevance to radioelement transport in soils and rocks have been undertaken only to a limited extent. Clays, zeolites, and carbonates, for example, have not been studied in relation to their surface complexation properties in any detail. Furthermore, even had the surface complexation properties of the mineral been investigated, it is not feasible to use measurements on individual minerals to predict the sorption behavior of mineral aggregates such as soils or rocks.

The formulation of a surface complexation model assumes experimental characterization of the adsorbent properties under conditions in which the substrate is a dilute suspension in the aqueous phase. However, with increasing concentration of the suspension, particles come into contact with each other and modify the apparent surface properties of the adsorbent. Still greater effects have been observed when two different adsorbents are mixed. It would have been advantageous if the sorption properties of an aggregate of different adsorbents had been additive, obeying the so-called linear adsorptivity model. However, experimental studies reported by Honeyman (1984 [DIRS 164878]) reveal that major nonlinear effects on adsorption are sometimes observed with mixtures. The linear adsorptivity model may therefore be an exception rather than the rule.

To overcome the practical limitations of surface complexation models, Davis et al. (1998 [DIRS 154436]) formulated a semi-empirical version of a site complexation model with limited parameterization, which represents a considerable advance over empirical isotherm formulations. Their approach could, with further refinement, finally realize a suitable model for predicting species adsorption under field conditions.

11.3 MATHEMATICAL MODEL

11.3.1 Approximations and Simplifications

The advantage in assuming a linear isotherm for a given radioelement lies in its simplicity of measurement, and in the ease with which the term can be incorporated into hydrological models, where it is assumed that all other geochemical parameters except the concentration of the sorbent remain invariant. Under these conditions, experimentally determined K_d values from the laboratory can be used for approximate predictions of radionuclide migration, provided that the host rocks have identical composition and properties per unit mass, and thus temperature and aqueous phase composition are identical and remain invariant. Without such constraints, predictions of radionuclide transport in the natural environment will be subject to large and unpredictable errors (Reardon 1981 [DIRS 154434]). Table I-1 modified after Apps et al. (1977 [DIRS 164864]) and Apps (1992 [DIRS 165225]), provides a very general estimate of potential uncertainties introduced through the application of experimental laboratory K_d values to radionuclide sorption in the field. The values given are only estimates, actual deviations being almost impossible to quantify.