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SECTION 194.14: ASSESSMENT OF K_d S USED IN THE CCA

**U. S. ENVIRONMENTAL PROTECTION AGENCY
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1.0 INTRODUCTION

The Title 40 Code of Federal Regulations (CFR) 194 requires U.S. Department of Energy (DOE) to conduct performance and compliance assessments evaluating the radioactive waste containment capabilities of the Waste Isolation Pilot Plant (WIPP). DOE has submitted to the U.S. Environmental Protection Agency (EPA) the WIPP Compliance Certification Application (CCA) in which DOE discusses this issue. The WIPP is a potential geologic repository mined in a thick salt unit called the Salado Formation. As part of this evaluation, DOE is to examine scenarios associated with drilling into the WIPP and subsequent release of radionuclide-bearing brines into geologic strata above the Salado Formation. The Rustler Formation is the geologic formation directly above the Salado Formation, and contains geologic strata in which radionuclides could be transported laterally with groundwater if released by a drilling event. The Culebra Member (Culebra) of the Rustler Formation is the most transmissive unit of the Rustler Formation, and is therefore the unit in which actinide movement would probably more readily occur in the event of a drilling intrusion into WIPP.

After radionuclides enter the Culebra, lateral transport of radionuclides within the groundwater in this rock unit is governed by many factors, including the ability of the native rock material to adsorb actinides onto rock surfaces, and potentially incorporate the actinides into mineral structures. This actinide sorption is described by a parameter called the " K_d " (or distribution coefficient), which is the subject of this report. The mathematical formulation of this chemical retardation process is described later in this report.

The DOE, EPA, the State of New Mexico, and other stakeholders have long recognized the potential importance of radionuclide transport within the Culebra. DOE has conducted numerous K_d -related studies over the years (refer to Appendix MASS, Attachments 15-1 through 15-3). The DOE entered into an agreement with the State of New Mexico in 1988, wherein the DOE agreed to develop data for K_d s used in the final performance assessment. DOE conducted additional K_d -related assessments and experiments. DOE's K_d -related study results acquired prior to completion of CCA-related calculations are presented in Appendix MASS, Section 15, and Attachments 15-1 through 15-3, and 15-6 through 15-10. These K_d experimental results and determinations of K_d ranges for the actinides were described in a memorandum from Larry Brush to Martin Tierney, dated June 10, 1996 (Brush, 1996a). Additional information and analyses relative to K_d s have been performed by DOE subsequent to the October 29, 1996 submission of the CCA, including a July 24, 1996 memorandum from Larry Brush to Martin Tierney in which the K_d ranges were revised, although the revised data was not submitted in time for use in CCA calculations (Brush, 1996b, WPO No. 41561). The results of DOE's additional work were presented in a July 30, 1997 information exchange between DOE and the Environmental Evaluation Group (Letter from G. Dials to R. Neill, Docket No. A-93-02, II-D-115).

The purpose of this document is to address the following issues:

- ◆ Discuss general application of the K_d concept.

- ◆ Are the K_d values used by the DOE in performance acquired through sound methodologies?
- ◆ Are experimental results adequate for use in PA?
- ◆ Are K_d values used by DOE consistent with those found in other data sources?
- ◆ Is the DOE's K_d distribution appropriate?

The report is organized into six sections, Section 1.0 being this introduction. The basic theory and application of K_d s to radionuclide transport are presented in Section 2.0. Section 2.0 also identifies the specific radionuclides (actinides) included in CCA and also includes a brief description of the Culebra actinide transport conceptual model. Section 3.0 presents a summary of the primary K_d data sources assembled or derived by DOE and the subsequent data used by DOE to derive the CCA's K_d values. Strategies for addressing the nature of radionuclides (actinides) entering the Culebra (i.e., actinide oxidation state distribution) and subsequent brine mixing in the Culebra are also presented in Section 3.0.

Section 4.0 includes the methodology and results of the K_d -related experiments conducted by DOE and its contractors, EPA's comparison of K_d values and ranges derived from these experiments with other data sources, and EPA's assessment of K_d distribution used in the CCA.

Section 5.0 summarizes the implementation and results of the CCA's transport model for the Culebra, as well as results of the performance assessment verification testing (PAVT) that was performed by DOE. Section 6.0 presents EPA's conclusions of this assessment with respect to the acceptability and representativeness of the K_d ranges and probability distributions used in the CCA transport model.

2.0 K_d THEORY AND APPLICATION

2.1 DEFINITION OF K_d

Chemical partitioning of a solute (i.e., actinide) between the liquid (groundwater) and solid (rock) phases in a groundwater flow system is often represented through the use of a distribution coefficient, or K_d . The K_d , also referred to as a sorption coefficient or a matrix distribution coefficient, is an empirical parameter defined as the ratio of the concentration of the solute on the solid to the concentration of the solute remaining in solution (i.e., groundwater), represented by the equation (Freeze and Cherry, 1979):

$$K_d = C_s / C_l$$

where C_s = mass of solute on the solid phase per unit mass of that solid phase
 C_l = concentration of solute in solution (i.e., groundwater)

The K_d defined by this equation is a linear isotherm, meaning that there is a linear relationship between C_s and C_l . Measured K_d values are typically reported in units of milliliters per gram (ml/g).

The K_d is a combined measure of the various processes (discussed below) that cause the retention of a solute within and on a solid matrix of geologic material. Values of K_d for specific solutes are generally measured in laboratory experiments through determinations of C_s and C_l after some period of equilibration, although both can also be derived from sorption studies performed in the field. Measured K_d s are generally considered to be a gross indication of all processes that cause the retention of a solute on the surfaces of various solid substrates (Freeze and Cherry, 1979). However, measured K_d s are usually not definitive of purely adsorption reactions in that other processes, such as ion exchange, co-precipitation, and redox changes, also affect the measured K_d values determined for any given set of conditions (Stumm, 1992).

Primary assumptions underlying the distribution coefficient approach to representing chemical partitioning in groundwater flow systems are that 1) the reactions that cause partitioning of solutes between the liquid and solid phases are completely reversible, and 2) these reactions are very fast relative to the rate of groundwater movement.

The transfer of a solute by adsorption or other chemical processes from the liquid (groundwater) to the solid (rock) phase retards the migration of that solute with respect to the rate of groundwater movement. The relationship of the K_d to the retardation of solute migration is expressed by the following equation (Freeze and Cherry, 1979):

$$R = V_w / V_s = [1 + (bK_d/n_e)]$$

where R = retardation factor

V_w = average linear velocity of groundwater movement

V_s = average linear velocity of the solute movement
 b = average matrix bulk density
 n_e = effective porosity of the matrix

This equation indicates that the higher the value of K_d , the greater the proportion of solute that is retained onto the solid matrix and the greater the retardation of that solute with respect to migration in groundwater. Solutes that have high K_d values are relatively immobile in groundwater flow system, whereas a K_d of zero would imply that the solute would migrate at the same velocity as groundwater.

2.2 FACTORS THAT AFFECT ACTINIDE K_d S

As previously discussed, the K_d is a combined measure of various processes that cause the retention of a solute within and on a solid matrix. As such, the K_d for a specific actinide is a function of the physical and chemical characteristics of the actinide, as well as the solution and the porous media through which the actinide is moving. An analogy to this is hydraulic conductivity, which is dependent on properties of the fluid as well as the media through which the fluid passes.

Characteristics of the actinide that can affect the K_d include oxidation state, aqueous speciation, and concentration. Characteristics of the solution that may affect actinide K_d s include pH and redox (Eh) conditions, $\text{CO}_2(\text{g})$ partial pressure, salinity, ionic strength, presence of competing cations, and the presence of organic ligands (Brush, 1996a; Brush, 1996b). Primary characteristics of the solid matrix that affect actinide K_d s include the surface area per unit mass (specific surface area), mineralogy, and the presence of coatings on mineral surfaces, such as iron, manganese, and aluminum oxyhydroxides, although adsorption to some extent can occur for any type of mineral surface. In general, actinide K_d s are higher under reducing, high pH conditions and when the surface area per unit of liquid is high (Novak et. al, 1996). Conversely, actinide K_d s are generally lower under oxidizing, low pH conditions, and when the surface area per unit of liquid is low.

2.3 APPLICATION OF K_d S TO ACTINIDE TRANSPORT IN THE CCA

The application of K_d s to contaminant transport is a common concept applied to many aspects of contaminant migration. Freeze and Cherry (1979, p. 403) state that K_d s are “widely used in studies of groundwater contamination. K_d is a valid representation of the partitioning between liquid and solids only if the reactions that cause the partitioning are fast and reversible and only if the isotherm is linear. Fortunately, many contaminants of interest in groundwater studies meet these requirements”. In the case of WIPP, sorption rates are assumed to be rapid and reversible, and the sorption isotherms linear over the extremely low concentration ranges expected for the actinides in the repository environment, consistent with the criteria for applicability outlined in Freeze and Cherry (1979). Domenico and Schwartz (1990, p. 442) state that “modeling sorption with a single parameter K_d is the most common approach. One of the most concerted efforts to apply this model was for the evaluation of geologic units as potential

host rocks for nuclear wastes. The extent to which sorption retards the spread of radionuclides has an extremely important bearing upon the suitability of a given site". Table 12.7, page 442 presents Domenico and Schwartz's estimated K_d values for 23 different radionuclides in salt, emphasizing that even in text book literature, the importance of K_d s relative to salt host rock, such as the WIPP, is well recognized.

Sorption of contaminants is a very common occurrence and in fact, is typically problematic from a remediation perspective because contaminants with high K_d s cannot be easily removed from the aquifer matrix. Remediation methods, such as pump and treat systems for groundwater, must take into account the types of contaminants present and sorption characteristics (Fetter, 1993). The fact that contaminant sorption is such a major issue in remediation underscores the pervasive importance of sorption and the commonly accepted concept of sorption in natural systems.

Adsorption is an important retardation mechanism with respect to actinide transport in a groundwater flow system. The K_d approach to representing chemical partitioning in groundwater flow systems was incorporated into CCA models to address the effect of adsorption on actinide transport in the event that a brine containing actinides is released to the Culebra Formation. As a prerequisite to the development of numerical models to address actinide transport in the Culebra, DOE specified those actinides that were of interest with respect to the CCA and would be included in the transport models. After that determination was made, a range and probability distribution of K_d s for each actinide of interest was developed by DOE from experimental data. Prior to the development of a numerical model, a conceptual model was developed to describe the physical and chemical transport processes in the Culebra.

Actinide transport in the Culebra was simulated under the CCA using the codes SECOFL2D and SECOTP2D (Ramsey, 1996). SECOFL2D is a two-dimensional groundwater flow model capable of simulating transient and steady state flow in porous media. SECOTP2D is a two-dimensional dual porosity transport model capable of simulating transport of radionuclides through fractured porous media.

The conceptual model and the criteria for selection of actinides of interest are briefly described in this section, but are discussed more thoroughly in **CARD 23 -- Models and Computer Codes**. The experiments used to develop the K_d ranges used in PA and probability distributions are summarized in Section 3.0 of this report. Application of actinide K_d s to the CCA transport models and the results of those models are presented in Section 5.0 of this report.

2.3.1 Actinides Used in the Transport Model

The DOE considered twenty-nine radioisotopes for CCA calculations, based on the inventory content and 40 CFR 191 requirements. To reduce the calculation burden, DOE made three assumptions to decrease the number of radioisotopes included in the numerical codes that compute indirect releases (i.e. NUTS, CCDFGF, and SECOTP). These assumptions are:

- ◆ Because of the small difference in mass between isotopes of the same element, it was assumed that the K_d measured for one isotope can be applied to any other isotope of the same element (Brush, 1996a; Brush, 1996b).
- ◆ Based on the inventory and high ranking in terms of EPA normalized releases relative to other isotopes and because of their long half-lives relative to the 10,000-year regulatory framework for containment, the list was narrowed to four radioisotopes to be considered for groundwater transport (^{239}Pu , ^{241}Am , ^{234}U , and ^{230}Th) and four possible oxidation states (+3, +4, +5, and +6).
- ◆ Based on the assumption that actinides with the same oxidation state have similar aqueous chemistry characteristics, in some cases K_d s determined for an actinide in one oxidation state were used to represent K_d s for other actinide of the same oxidation state.

The ranges of K_d s and probability distributions for each of these four isotopes (in the appropriate oxidation states) were required to evaluate actinide partitioning between solid and liquid phases within the Culebra as part of the transport simulations. The K_d ranges and probability distributions used by DOE are presented in Section 3.0 of this report.

2.3.2 Conceptual Model for Actinide Transport in the Culebra

The conceptual model developed by DOE for actinide transport in the Culebra is summarized below, and is more thoroughly addressed in Chapter 6 of the CCA. EPA's review of DOE's conceptual models can be found in the Technical Support Document for Section 194.23 Models and Computer Codes (A-93-02, V-B-6).

In the vicinity of the WIPP site, the Culebra is the most transmissive unit in the Rustler Formation and is therefore considered to be the most likely pathway for subsurface transport of actinides released to groundwater as a result of borehole intrusions of the repository (Rechard, 1995). The Culebra is a regionally persistent geologic unit and is present above the entire WIPP site. The Culebra is conceptualized as a fractured medium with a median total porosity of 0.16 (Meigs and McCord, 1996 -WPO# 37450). Groundwater flow in the Culebra is generally to the south and occurs predominately in the lower, more transmissive portions of the unit (Beauheim and Holt, 1990). The highest transmissivities in the WIPP site are in the southeast portion of the site.

The physical character of the Culebra with respect to groundwater transport is conceptualized as having dual porosity¹ (e.g., flow occurs in both rock fracture and rock matrix). The medium is conceptualized as consisting of 1) advective porosity, where solutes are carried by groundwater flow in fractures, and as 2) fracture-bounded zones of diffusive porosity, where solutes move through a rock matrix via slow advection or diffusion (Holt, 1997). The advective porosity incorporates interconnected fractures and vugs and irregular interbeds of silty dolomite. The diffusive porosity predominately represents the porosity of the dolomite matrix. Actinide transport is retarded both physically and chemically when diffusion out of the advective porosity and into the dolomite matrix occurs. Physical retardation occurs because actinides that diffuse into the matrix are essentially removed from transport by advective groundwater flow, at least until the actinides diffuse back into the advective porosity. Chemical retardation occurs within the rock matrix as a result of adsorption of actinides onto the surfaces of dolomite or other mineral grains. The relationship between the sorbed and liquid concentrations of actinides is represented by its K_d value. In the transport codes, the distinction between advective and diffusive porosity is important because partitioning of actinide to the dolomite by sorption is considered only for the groundwater migrating through diffusive porosity zones.

Transport behavior in a double porosity medium varies as a function of advective travel length and travel time. At small time and length scales, the behavior fits a single porosity model with transport occurring entirely in the advective (fracture) porosity, because solutes do not have enough time to diffuse or be advected into the matrix of the dolomite rock. At larger length and time scales solute transport behavior in the Culebra is more aptly described using a double porosity model. Given sufficient time, solutes access the diffusive porosity via diffusion or slow advection so that some amount of actinide attenuation occurs, but transport through fractures also occurs. Finally, at very large length and time scales, Culebra behavior again responds as a single porosity model, but this time with transport in both advective and diffusive porosity. This scaled response is significant with respect to actinide attenuation because the specific surface area per unit mass of the diffusive porosity is much greater than in the advective porosity (Holt, 1997).

¹While the Culebra is conceptualized as a dual-porosity medium for transport purposes, this may be a conservative assumption for use throughout the WIPP region. Well tracer test data (CCA Reference 343) indicate that the Culebra may better be considered as a single (matrix) porosity rock unit in some areas near the waste panel area. In this matrix porosity case, fractures do not apply and all flow and transport is through the matrix. This provides greater physical retardation for actinides than the dual-porosity case.

3.0 SOURCES OF K_d DATA USED BY DOE IN THE CCA

Ranges of K_d values were developed by DOE for specific actinides modeled in the CCA. These ranges were based on experimental studies performed by DOE (and its contractors) and applicable literature. This section presents a summary of the primary sources of data used to derive the K_d ranges. Strategies used by DOE for addressing oxidation state of actinides introduced to the Culebra and brine mixing in the Culebra are also presented in this section.

As indicated in Section 2.0, DOE derived K_d values for four actinides, representing six oxidation states: Pu-239 (Pu III and IV), Am-241 (Am III), U-234 (U IV and U VI) and Th-230 (Th IV). The strategy implemented by DOE to develop K_d ranges for these actinide was to first establish experimentally obtained K_d ranges for Am(III), U(VI), Th(IV), and Np(V), and then to use an oxidation-state analogy to extrapolate this range to represent Pu(III), Pu(IV), U(IV), and Np(IV) (Brush, 1996a; Brush, 1996b). From this work DOE derived the K_d values for the Am(III), Th(IV), Np(IV and V), Pu(III and IV), and U(IV and VI) used in PA (Appendix PAR, Parameters 52 to 57).

3.1 RANGES AND PROBABILITY DISTRIBUTIONS OF ACTINIDE K_d S

Brush (1996a; Brush, 1996b) provides ranges and probability distributions of matrix distribution coefficients for dissolved Pu(III and IV), Am(III), U(IV and VI), Th(IV), under conditions expected during transport in the Culebra. (Refer to Section 3.2 of this report for discussion of why specific oxidation states for multiple oxidation state actinides were selected.) The ranges for these actinides were revised from an earlier submittal (compare Brush, 1996a to Brush, 1996b), however, the unrevised ranges were used in the CCA because the revised ranges were apparently not available in time for inclusion in CCA calculations. EPA reviewed both papers and values presented therein. The K_d data for Pu, Am, U, Th were required for the PA calculations in support of the WIPP CCA (Garner, 1996). The K_d data were provided for Np in the event that these data were needed in sensitivity analysis calculations for the PA (Brush, 1996a; Brush, 1996b). The proposed ranges were derived from the DOE's Retardation Research Program and related aspects of the PA using empirical (batch) sorption, mechanistic sorption and column-transport derived data as described below (Appendix MASS 15.1). A uniform distribution was recommended by Brush (1996a; Brush, 1996b) as appropriate for use in the PA based on the narrow range of values (less than three orders of magnitude), and the uncertainty associated with possible conditions in the Culebra (brine type, partial pressure of $\text{CO}_2(\text{g})$ and resulting pH).

According to Brush (1996a; Brush, 1996b), the primary source of actinide K_d measurements was the experimental work by Triay and coworkers at Los Alamos National Laboratory. Triay conducted experiments on sorption of Pu(V), Am(III), U(VI), Th(IV), and Np(V) on crushed dolomite rocks from the Culebra using different brine compositions, various $\text{CO}_2(\text{g})$ partial pressures and varying actinide concentrations.

The experimental procedure used by Triay involved crushing Culebra rock samples to obtain the 75 to 500-um size fraction. This fraction was washed by dilute HCl and then pre-treated with the brine solution prior to the introduction of actinides. This procedure was used to minimize imprecision resulting from variabilities in surface chemical properties and to remove the clay-sized fraction. Experiments were conducted using four different synthetic brine types representative of potential conditions that might occur in the event of a release from the WIPP repository. The fluids used were representative of a Salado brine (Brine A), a Castile Formation brine (ERDA-6), and Culebra brines (AISinR and H17). The effects of partial pressure of CO₂(g) on sorption were evaluated from experiments conducted over the range of values expected for Culebra groundwater ($10^{-3.5}$, $10^{-2.73}$, $10^{-1.98}$ and $10^{-1.5}$ atm). The effects of equilibration time on sorption and desorption were evaluated by conducting experiments over 3-day, 1-, 3-, 6-, and 8-week time periods. The effects of dissolved actinide concentration were evaluated in the 6-week experiments by determining K_d s over a range of dissolved actinide concentrations.

Results of the 6-week Triay experiments using a CO₂(g) partial pressure of $10^{-3.5}$ atm for the deep brines and CO₂(g) partial pressures from $10^{-3.5}$ to $10^{-1.98}$ atm for the Culebra brines established the initial range of K_d values for Pu(V), U(VI), Th(IV), and Np(V) (Brush, 1996a; Brush, 1996b). A K_d range for Am(III) was not developed from the Triay experimental data because of an observed relationship between K_d s and the final dissolved concentration of Am(III). This relationship indicated that processes other than sorption to the matrix were occurring within the Am(III)- K_d experiments (Brush, 1996a; Brush, 1996b). As a result of the failure of the Am(III)- K_d experiments, DOE chose to use experimentally obtained ranges for Pu(V) K_d s to represent Am(III) K_d s in the CCA modeling (Appendix MASS, Attachment 15-1, 15-2). This decision by DOE is based on the assumption that K_d s for Am(III) are greater than or equal to those for Pu(V), therefore use of the Pu(V) value would be conservative. Furthermore, the K_d range established for Th(IV) in the deep brine was used for the K_d range of Th(IV) in the Culebra because the data from the Th(IV) Culebra brine experiments did not meet certain experimental control criteria. Some of the initial K_d ranges established from the Triay experiments were revised based on the results of additional experimental studies, as described below.

The DOE conducted a mechanistic study on sorption of Am(III), U(VI), Th(IV), Pu(V), and Np(V) on a Norwegian dolomite under a variety of ionic strength solutions (0.05, 0.5, and 5.0 M NaCl). The experiments were conducted with headspace CO₂(g) concentrations of atmospheric, 0.5% and 5%, and under a range of pH (from 3 to 10 standard units). Although this study did not yield Culebra-specific K_d data, the results were used to extend some of the empirical data from the Triay deep brine experiments to the alkaline pH conditions anticipated from the use of an MgO backfill in WIPP disposal rooms. The lower end of the K_d range for U(VI) was decreased and the upper end of the K_d range for Np(V) was increased based on the results of the mechanistic study (Appendix MASS, Attachments 15-1, 15-2).

Brush (1996a; Brush, 1996b) also reports the results of experimental studies of actinide

transport through cores obtained from the Culebra in the WIPP Air Intake Shaft. These experiments included spike and, in a few cases, continuous injections of Am(III), Th(IV), Np(V), Pu(V), and U(VI) in synthetic Culebra and deep brines into the cores. Additional brine was pumped into the cores at low flow rates (less than 0.1 ml/min) for periods of up to 237 days. The effluent was continuously collected and periodically analyzed by gamma spectrometry or liquid scintillation counting (LSC). DOE did not directly determine K_d s from these experimental results. Instead, values of the retardation factor were calculated from the observed delay between the elution peaks of non-adsorbed radionuclides and those of U and Np. Values of K_d s were then back-calculated from the retardation factor and the experiment-derived porosities. Breakthrough was not observed for Pu, Am, and Th (letter from G. Dials to R. Neill, Attachment 2, A-93-02, II-D-115). Minimum K_d s were calculated for these strongly retarded actinides. The lower end of the K_d ranges for U(VI) and Np(V) were decreased based on the results of the intact core study (Appendix MASS, Attachment 15-1, 15-2 and Brush, 1996a; Brush, 1996b).

The post-test cores used in the column experiments were examined to determine the distributions of Pu(V) and Am(III) as a function of distance from the influent ends. These results were presented to EEG in the presentation by W. G. Perkins and Lucero, July 30, 1997, Albuquerque, New Mexico (Letter from G. Dials to R. Neill, A-93-02, II-D-115)). The Am(III) was found to nearly all be present in the top 1 mm of the core, implying that it had been attenuated by a precipitation reaction as suggested in this comment. Depending on the solubility of the Am(III) solid precipitated, the solution concentration would have been decreased, but some amount of Am(III) would have been left in solution and available for transport through the column, as suggested by the low concentrations in the solid phase beyond 1 mm from the influent end. However, no Am(III) was detected in the effluent solution, indicating that all of the Am(III) was effectively attenuated.

The concentration profile for Pu(V) showed a more smeared out concentration gradient from the influent end that is suggestive of sorption attenuation processes. Based on these results, Perkins and Lucero calculated minimum K_d s in the range of 175 to 282 ml/g for Pu(V) and 190 to 327 ml/g for Am(III). These K_d values are within the range of 20 to 500 ml/g determined for Pu(V) in batch experiments as reported by Brush (1996a; Brush, 1996b).

3.1.1 K_d Ranges Derived from Oxidation State Analogies

Oxidation state analogies were used by DOE to define the K_d ranges for Pu(IV), U(IV) and Np (IV). The analogies are based on the assumption that actinides in the same oxidation state exhibit similar trends and behaviors and that these trends allow the behavior of one actinide in a particular oxidation state to be estimated from or bounded by the behavior of another actinide in the same oxidation state (Nowak, 1997, presentation summarized in letter from G. Dials to R. Neill, Attachment 2 A-93-02, II-D-115). Based on this analogy, predicted adsorption of an early (lower atomic number) actinide series element is used as a lower bounding estimate for adsorption of a late (higher atomic number) actinide series element in the same oxidation state. For example, the K_d range for Th, which is the first actinide series element, should have the

lowest K_d values among the actinides in the a (IV) oxidation state. Therefore the experimentally derived K_d range for Th (IV) was used as the K_d range for Pu(IV), U(IV) and Np (IV) (Brush, 1996a; Brush, 1996b).

Nowak (1997), cited work by Silva (1995) that showed the following relationship between oxidation state and average K_d for a number of actinides on an assortment of minerals:

$$(IV) > (III) > (VI) > (V).$$

These results and other empirical data support the use of the K_d range developed for Pu(V) as a lower bound for Am (III). By the oxidation state analogy, Am(III) chemical behavior is quantitatively similar to Pu(III) chemical behavior and therefore the K_d range developed for Pu(V) was also extrapolated to Pu(III) as a conservative lower bound (Nowak, 1997).

3.2 OXIDATION STATE DISTRIBUTIONS FOR ACTINIDES

The oxidation state of an actinide can significantly affect the extent to which it is partitioned to solid surfaces (Nowak, 1997). To establish ranges and probability distributions of actinide K_d s for use in the PA calculations, the oxidation-state distributions of the actinides of interest were first predicted by DOE. Of the actinides for which K_d data are required for the PA calculations, Am and Th have only one possible oxidation state under the low temperature conditions anticipated at the repository. However Pu, U and Np² each have more than one possible oxidation state under those conditions.

DOE conducted laboratory studies under expected WIPP conditions to predict oxidation state distributions of Pu, U, and Np in deep Castile and Salado brines. The results of the study, as well as other previously published results regarding projects other than the WIPP Project, predicted that Pu will be present predominantly as Pu(III) and Pu (IV) but not as Pu(V) or Pu(VI), U will be present as U(IV) and U(VI), and Np will be present as Np(IV) and Np(V) under expected repository conditions.

Stockman (1996) performed a modeling study to evaluate the applicability of the DOE oxidation state prediction to expected conditions in the Culebra. Results of the study showed the Culebra fluids have limited capacity to either oxidize or reduce actinide elements. Based on these findings, Brush (1996a, 1996b) stated it was “reasonable to assume that the oxidation state distributions of Pu, U, and Np predicted for WIPP disposal rooms will be maintained along the entire off-site transport pathway”.

For any given vector in the PA, solubilities were calculated for Am (III), Th (IV), , as well as either Pu(III) or Pu(IV), U(IV) or U(VI), and Np(IV) or Np(V). The PA specified the oxidation state of the actinides with more than one possible oxidation state by sampling

² Np is not used in transport calculations.

OXSTAT, a parameter with a uniform probability distribution of 0 to 1. If the sample value of OXSTAT was 0.5 or less, the PA used solubilities predicted for Pu(III), U(IV), and Np(IV). If OXSTAT was greater than 0.5 then PA used solubilities for Pu(IV), U(VI), and Np(V).

In June and July of 1996, DOE repeated the procedures used to establish K_d ranges described in Brush (1996a) using revised empirical-sorption, revised mechanistic sorption, and original transport data (Brush, 1996b). This reassessment (Brush, 1996b) indicated that revised K_d ranges were in order, but DOE concluded that although it was “too late for performance assessment (PA) personnel to rerun their transport calculations with the revised ranges...PA can still use these K_d s to assess the impact of the erroneous values on their calculations. Based on our discussions with them, we do not expect any significant impact” (Brush, 1996b).

3.3 BRINE COMPOSITION IN THE CULEBRA

Brine composition can also affect the partitioning of actinides. The extent to which brines from the Salado and Castile will mix with the Culebra under possible intrusive scenarios was an important consideration by DOE in developing an appropriate range and probability distribution of actinide K_d s. However, predicting the degree of mixing that may occur under different repository scenarios and applying the appropriate weighting factor to the K_d ranges was described as overly complex by DOE. To circumvent this problem, DOE established separate K_d ranges for deep brine (Salado and Castile) and shallower Culebra brines for each actinide (including the appropriate oxidation states). DOE then used the K_d range and distribution that resulted in the least retardation for each element or elemental oxidation state in the PA (Brush, 1996a; Brush, 1996b). This approach is reasonable and provides for incorporating the highest levels of actinide mobility in the PA calculations.

3.4 FIELD TRACER TEST EXPERIMENTS

Field tracer tests were conducted at the WIPP to further characterize physical transport in the Culebra and support the conceptual model (Meigs, 1996; Jones et. al., 1992). Recent tracer tests were conducted at Hydropads H-11 and H-19 and included single well injection-withdrawal tests and multi-well convergent-flow tests. Fluoro-and chlorobenzoic acids and iodide were used as tracers. The results of the tracer tests did not provide actinide K_d values. However, DOE concluded from the test results, that transport does not only occur in the advective porosity as there is significant diffusion and advection in the matrix. Transport through the rock matrix makes more mineral surface area available for the uptake of actinides by adsorption reactions relative to a situation in which the bulk of the water is moved only through rock fractures.

3.5 EXPERIMENTS ON IMPACTS OF ORGANIC LIGANDS

Brush (1996a; Brush, 1996b) conducted experiments to evaluate the effects of organic ligands on actinide K_d s under conditions expected in the Culebra. Organic ligands included in the experiments were acetate, citrate, ethylene-diamine-tetraacetic acid (EDTA), and lactate. The actinides included in the experiments were Pu(V), Am(III), U(VI), Th(IV), and Np(V). The first experiments were conducted using a deep brine and a Culebra brine with low, intermediate and high concentrations of the organic ligands. The range of concentrations used in the experiments bracket the predicted concentrations of organic ligands within the brines in the repository. Results of the experiments indicate that at relatively low concentrations of the organic ligands, the K_d s of the actinides are not impacted. At high organic concentrations, however, the actinide K_d s are generally decreased, although the effect is mixed (Brush, 1996a; Brush, 1996b). The most notable effects were the reduction of approximately four orders of magnitude in the K_d of Th(IV) for even the low organic ligand concentration experiment. Brush (1996a, 1996b) states that the ranges and probability distributions of K_d s for Pu, Am, U, Th and Np were not revised on the basis of these experiments because large quantities of other metals will be present in the repository to form complexes with the organic ligands, preventing them from complexing with the actinides and thereby affect the K_d s. Preliminary equilibrium modeling under conditions anticipated in the repository indicates that 99.8% of the EDTA would complex with Ni (Brush, 1996a; Brush, 1996b). Likewise, equilibrium modeling of Th(IV) aqueous speciation under conditions controlled by MgO backfill reactions, implies that the organic ligands would be predominantly complexed by Ca and Mg rather than actinides. These model calculations imply that organic ligands are unlikely to have an appreciable impact on actinide K_d s as a result of actinide complexation reactions.

3.6 K_d RANGES RECOMMENDED BY DOE FOR THE PA

The ranges recommended for use in the PA are presented in Table 1. The PA was conducted using the initial K_d ranges noted on this table because the revised ranges in parenthesis were not received in time to be implemented prior to the October, 1996 PA submission. Brush (1996a; Brush, 1996b) stated that the DOE does not anticipate that significant changes in the normalized releases would result from implementation of the revised K_d ranges compared to the initial ranges.

4.0 EVALUATION OF K_d DATA

This section presents EPA's evaluation of the K_d data used in the CCA calculations of actinide transport in the Culebra. The evaluation includes an assessment of the methodology and results of the experiments conducted by DOE and its contractors, a comparison of K_d values and ranges derived from those experiments with other data sources, and a discussion regarding the K_d distribution used in the CCA.

4.1 ASSESSMENT OF DOE EXPERIMENTS

According to Brush (1996a, 1996b), the primary source of actinide K_d measurements was the experimental work by Triay and coworkers at Los Alamos National Laboratory (Empirical Sorption Study). Additional experimental work by Brady and Lucero (Brush, 1996a; Brush, 1996b) at Sandia National Laboratory was used to augment the results of Triay, where appropriate. Reports by these various scientists are not cited by Brush (1996a, 1996b), hence it was not possible to conduct critical reviews of their separate experimental methodologies.

EPA notes that Triay's work, for the most part, appears to be the primary study used to define K_d values representative of actinide retention by the Culebra dolomite. Triay conducted experiments with different brine compositions covering the range of possibilities expected in the event of a release from WIPP under different scenarios. DOE believes, and EPA concurs that the compositions of the electrolyte solutions can be expected to be the most important factor affecting the variability of K_d s (Dosch and Lynch, 1980; Sheppard and Thibault, 1990). Also, Triay used crushed dolomite rock from the Culebra formation so that site-specific material was used.

According to Brush (1996a, 1996b), Triay's experimental procedure involved crushing Culebra rock samples to obtain the 75 to 500- μm size fraction. This fraction was washed by dilute HCl and then pre-treated with the brine solution prior to introduction of actinides. This type of procedure is often used in K_d or adsorption experiments to minimize imprecision resulting from variabilities in surface chemical properties.

EPA determined that the initial actinide concentrations in experimental brine effluent appear to be about an order of magnitude less than the solubilities of any actinide solids that might be expected to form under the experimental conditions, although the results of such calculations are not presented by Brush (1996a, 1996b). That is, the experimental brines were undersaturated with respect to potential actinide solids. EPA believes that this check is important to ensure that losses of actinide from solution are caused by adsorption processes rather than precipitation reactions. As a result, EPA concludes that changes in actinide concentrations observed were most likely a result of adsorption reactions rather than precipitation of actinide solids.

EPA concluded that there are four areas that were not completely addressed by Brush

(1996a, 1996b) in his descriptions of Triay's work. First is the question as to whether steady-state conditions were reached in the K_d experiments. Triay collected samples after variable equilibration times (e.g., 3 days, 1 week, 2 weeks, 3 weeks, 6 weeks, and 8 weeks), but the results of these time-series experiments are not discussed by Brush (1996a, 1996b). Instead, only the 6-week results were used to define K_d s without any discussion of the time-series experiments. Equilibration times of 48 hours or less are often considered sufficient for K_d experiments, but Brush (1996a, 1996b) provided no discussion of this subject. Although no discussion is provided regarding time trend data, EPA believes it is likely that steady-state conditions were achieved given the relatively long equilibration times of the experiments (i.e., 6 weeks).

Second, the effects of actinide source term concentration on the K_d s was not addressed, making it difficult to determine whether the experiments were conducted under conditions where a linear relationship between retention and concentration would be expected. Triay conducted experiments over small ranges of actinide concentrations, but the resulting isotherms were not provided or discussed in detail by Brush (1996a, 1996b). EPA notes that although evidence of linearity was not provided by DOE, under the experimental conditions of high pH, the adsorption densities of most aqueous cations, such as the actinides, tend to deviate from a linear dependence on concentration only with increases in their aqueous concentrations (Dzombak and Morel, 1990). Generally, nonlinear adsorption of solutes to a solid substrate only occurs at some concentration level above a threshold at which the highest energy adsorption sites are all filled. Actinide concentrations are not expected to reach these levels under conditions of solubility control by various actinide solids in the presence of the MgO backfill. More importantly, nonlinear adsorption is also operative in the opposite sense, that is, nonlinear desorption. In most aqueous-solid systems, solutes that are adsorbed are not desorbed at the same rate as they are adsorbed (Stumm, 1992). However, in DOE's modeling approach with K_d s, solutes that are adsorbed are assumed to be reversibly desorbed, as well. As such, EPA concludes that the use of K_d s to represent the reversible partitioning of actinides between the solid and liquid phases is reasonable and conservative for the extremely low concentrations of actinides expected for the chemical conditions of the subsurface as dictated by the low solubilities of the actinide solids.

Third, the effect of the magnesium oxide backfill in the repository for creating alkaline pH conditions in brines passing through it was not considered in the experimental design of Triay. Reactions between magnesium oxide, water, and carbon dioxide are expected to produce pHs from about 9 to 10, whereas the brines used by Triay had near-neutral pHs. However, EPA concludes that the adsorption of cationic species, such as for the dissolved actinides, generally increases with increasing pH, hence the reported values might be considered conservative with respect to changes attributable to pH. For example, Pu(IV), Pu(V), and Np(V) adsorption to iron oxyhydroxide [FeOOH] increase substantially at pH > 5 to 6 (Girvin et al., 1991; Sanchez et al., 1985). Similar observations have been made for Am and Np adsorption to various silicic rock types as a function of pH (Beall et al., 1980).

Less information is available in the literature on the adsorptive properties of dolomite,

and Brush (1996a, 1996b) does not provide any discussion on this subject based on information in the literature. However, EPA believes that dolomite [$\text{CaMg}(\text{CO}_3)_2$] would be expected to have surface charge characteristics that are similar to calcite [CaCO_3] for which a zero point of charge at pH 9.5 to 10 is reported (Doner and Lynn, 1989; Adamson, 1990). Thus, it might be expected that for the actinides (which form cationic solutes under most conditions), adsorption should be greater under the alkaline conditions produced by the magnesium oxide backfill than under the near neutral pH conditions of the brines used for the actinide K_d experiments, depending on the $\text{CO}_2(\text{g})$ partial pressure. However, the solubility of $\text{CO}_2(\text{g})$ increases with increasing pH, potentially resulting in increased carbonate complexing and hydrolysis of actinide species, which may decrease adsorption. It should be noted that the mechanistic experiments of Brady (1996) did evaluate the effects of higher pH on K_d values (Brush, 1996a; Brush, 1996b), but these experiments were performed on non-site specific materials (Norwegian dolomite).

Fourth, the K_d experiments for Am(III) failed for various reasons described by Brush (1996a, 1996b). Consequently, K_d s measured for Pu(V) were used to represent Am(III). Then, because Am(III) is the analogue for Pu(III), the K_d s measured for Pu(V) were also used to represent Pu(III). EPA concludes that this approach requires the extrapolation of one data set to represent two others, which increases the uncertainty of the results, but this was necessary given the constraints of the experimental program. Also, given the general trend in actinide K_d s for different oxidation state of (IV)>(III)>(VI)>(V), the use of a K_d determined for Pu (V) to represent Am (III) and Pu(III) is probably a conservative underestimate.

4.1.1 Negative K_d Results

In the reports by Brush (1996a), negative K_d values are reported for a small number of the experimental results. Bob Neill (A-93-02, II-D-117) raised concerns about the omission of negative K_d values in the development of K_d ranges for the actinides and the overall precision of the experimental results. Consequently, the negative K_d results were reviewed for each actinide to determine how and if they were used by DOE to determine K_d ranges that were input to the performance assessment.

Plutonium. Negative K_d s are reported by Brush (1996a) in Table B-5, page 28, for experiments conducted with Pu(V) and pure dolomite. According to this table, the negative K_d s occurred for experiments with pH values of 6.7, 4.05, 3.51, and 3.11. However, the only data considered from these experiments for determining K_d ranges for the CCA were for two experiments conducted at pH 9.87 and 9.88, for which K_d values of 349.56 and 410.9, respectively, were reported. These results were considered in the K_d range determination because they were relevant to the alkaline pH conditions expected from reactions with the MgO backfill. The K_d values at low pH (which are not expected in the Culebra), where the negative K_d values occurred, were not included in the K_d range determination for Pu(V).

Americium. One instance of a negative K_d for Am(III) was reported by Brush (1996a) in Table C-6, page 46. However, the experimental data from the K_d experiments with Am(III) were

not used to determine a K_d range for Am(III) in the CCA because trends in the results indicated that precipitation of Am(III) as a solid may have occurred as described by Brush (1996a). Instead, the K_d range determined for Pu(V) was used for Am(III), as well; hence, the single negative K_d reported never entered into any of the assessments used to determine the K_d range for Am(III).

Uranium. Negative K_d s for U(VI) occurred in a few of experiments reported by Brush (1996a). A single value of $K_d = -5.41$ ml/g for U(VI) was reported for experiment #12088 for Brine A and 1.4% CO₂(g) in Table D-1, page 52. However, only the experiments conducted with the ambient CO₂(g) level of 0.33% were used in determining the K_d range for U(VI); hence, this negative K_d did not enter into any K_d range determinations for U(VI).

A negative K_d of -1.66 ml/g for U(VI) in H-17 brine and 1.4% CO₂(g) (Experiment #12091) was reported in Table D-4, page 55 of Brush (1996a). This result was considered in the determination of the initial K_d range for U(VI) of -1.66 to 68.7 ml/g as described on page 50, third paragraph. However, the text by Brush (1996a) in that paragraph goes on to state that: “However, we set the lower limit of this range equal to 0 ml/g because there is no reason why a K_d could have a value less than 0.” This sentence indicates that the negative K_d determined experimentally was not included in the determination of the K_d range for U(VI) for the CCA. Other negative K_d s for U(VI) are also listed in Table D-4, but these occurred in experiments for which results were excluded from evaluations because of unacceptable differences between standards and controls.

One more negative K_d for U(VI) was reported by Brush (1996a) in Table D-5, page 57, for an experiment conducted with pure dolomite and 0.5% CO₂(g) at pH = 8.49. However, only the two experiments conducted at pH values of 9.88 and 9.87 were considered in the K_d range determination for U(VI), hence this negative K_d was excluded from the evaluation.

Among the actinides, determinations of negative K_d s by DOE occurred most often in the U(VI) experiments (Brush, 1996a). Thus, it has been suggested (Neill, A-93-02, II-D-117) that the lower bound for the U(VI)- K_d should be zero. However, the fact that the uncertainties in the analytical data did not allow a valid K_d to be calculated for some experiments is not a reason to assume that the K_d must be zero. Additionally, information in the literature indicates that K_d values for U(VI) and various minerals and rock types are generally low but not zero (McKinley and Scholtis, 1993; Sheppard and Thibault, 1990; Stenhouse and Pöttinger, 1994), particularly under the alkaline pH conditions produced by reactions with the MgO backfill, under which the surfaces of sorbents can be expected to become negatively charged, hence more conducive to the adsorption of cationic solutes (Dzombak and Morel, 1990). The lowest U(VI) K_d value that was determined in column experiments conducted by Lucero, as described by Brush (1996), was 0.03 ml/g. Based on the experimental results and information in the literature, a K_d of 0.03 ml/g for U(VI) is considered to be reasonable and conservative lower value for the K_d range for U(VI).

Thorium. No negative K_d s for Th(IV) were reported by Brush (1996a).

Neptunium. Three negative K_d s for Np(V) were reported by Brush (1996a) for experiments conducted with pure dolomite at pH = 5.81 and 3.11 (Table F-5, page 77) and at pH = 6.39 (Table F-5, page 79). However, only K_d s determined for pure dolomite at pH 9.88 and 9.87 were considered in the determination of the K_d range for Np(V); hence, the negative K_d s were not considered in the evaluation.

In summary, negative K_d s were reported by Brush (1996a) for all of the actinides except Th(IV). However, in all cases the negative K_d s were not included in the determinations of the K_d ranges for the CCA because 1) the experimental conditions were not considered representative of expected repository conditions; 2) the experimental data failed to meet quality assurance protocols; or 3) it was not considered to be a reasonable experimental result to have a negative K_d as a [i.e., U(VI)]. In fact, the determination of a negative K_d for an actinide in a batch experiment implies that there is some source of that actinide in the solids that dissolved to the extent that the solution concentration increased beyond the starting concentration. Experiments can produce this type of result when very low concentrations of the studied solute, such as for the actinides, are used to avoid the precipitation of solid phases. In such cases, the decrease in analytical precision near the detection limits for the actinides can give what appears to be a higher concentration in the final solution than in the initial solution, even though statistically or realistically, there is no real change in concentration. Basically, it is a problem of determining the difference between two very small numbers.

Overall, EPA considers that it would be unreasonable to include experimental results of negative K_d s in the determination of K_d ranges because that would imply that the Culebra dolomite is a greater source of actinides than the potential actinide source solutions. Consequently, EPA agrees that it is reasonable to base the lower end of the K_d ranges on the lowest positive K_d s determined in experiments representative of expected the chemical conditions as has been done by DOE.

4.1.2 Assessment of Organic Ligand Experiments

A series of experiments were conducted by Triay to determine the effects of different organic ligands expected to be present in the repository on actinide K_d s (see Brush, 1996a; Brush, 1996b, Appendix G). The organic ligands examined included acetate, citrate, EDTA and lactate. Experiments were conducted over a range of concentrations characterized as “low”, “intermediate”, and “high” (see Table G-1 in Brush, 1996a, 1996b). The results of these experiments are summarized in Section 3.0.

The results of the experiments with organic ligands were excluded by Brush (1996a, 1996b) in his derivation of actinide K_d ranges for input to performance assessment modeling. Brush (1996a, 1996b) hypothesized that under actual repository conditions, a surplus of cationic solutes (*e.g.*, Mg^{+2} , Ca^{+2} , Na^{+} , Fe^{+2} , Ni^{+2} , *etc.*) will be present and will form complexes with the organic ligands, making them unavailable for affecting actinide aqueous speciation. EPA concludes that this argument is consistent with the general chemical observation that reactions that promote hydrophilic behavior (*i.e.* formation of soluble ions in the aqueous phase) usually

cause decreased partitioning to the solid phase of those solutes through adsorption reactions. In the case of the actinide K_d s, the converse of this observation is relied upon by Brush (1996a, 1996b), as he assumed if actinide speciation is unaffected by the organic ligands, then the K_d s are likely to be unaffected as well.

DOE tested the validity of this hypothesis by comparing the aqueous speciation of the organic ligands in the experimental solutions to those expected in the repository. The ERDA6 brine was used to represent the background solution for the experimental conditions. The ERDA6 brine, modified to reflect equilibrium with halite, anhydrite, brucite, and hydromagnesite, was used to represent a background solution representative of expected repository conditions where reactions with MgO backfill will produce alkaline conditions. For both solutions, the concentrations of the actinides were taken from calculations of solubility equilibria for actinide solids under conditions expected for the repository (Table 2). The concentrations of the organic ligands were taken from those predicted for WIPP (Table G-1 in Brush, 1996a, 1996b). The FMT model (Version 2.2, FMT_970407_HMAG5424. CHEMDAT) was used to perform the speciation calculations (Novak et al., 1996; SNL, 1995).

Results from the speciation calculations are generally consistent with the hypothesis of Brush (1996a, 1996b), in that the percentages of organically complexed actinides are decreased under expected repository conditions relative to the experimental solutions (Table 3). The largest decrease was observed for Th(IV), one of the actinides whose K_d s are most affected by organic ligands according to the experimental studies of Triay. Compared to Th(IV), Am(III) showed only a small decrease in organic complexation under expected repository conditions relative to the experimental solutions. The proportion of organically complexed Np(V) was small in both solutions. All three actinides are predicted to have increased proportions of hydroxyl and carbonate species under expected repository conditions, consistent with the alkaline conditions resulting from MgO backfill reactions.

EPA notes that it is difficult to assess whether or not these speciation calculations are completely descriptive of the expected repository conditions. On one hand, competition for organic ligands would be expected to increase because of the presence of metals in the actual repository, thereby decreasing the amount available for complexing actinides as discussed by Brush (1996a, 1996b). Metals (e.g., Al^{+3} , Fe^{+2} , Ni^{+2} , Pb^{+2} , etc.) are not included in the FMT database so their effects on aqueous speciation could not be assessed. On the other hand, increased formation of negatively charged hydroxyl and carbonate actinide species under the alkaline conditions resulting from MgO backfill reactions may decrease specific adsorption. Neither of these two possibilities can be definitively described based on the results in Brush (1996a, 1996b).

However, EPA concludes that the results of the speciation calculations, consideration of K_d s reported in the literature, and expected increased adsorption under alkaline conditions, support the contention of Brush (1996a, 1996b) that the K_d ranges exclusive of the organic ligands should be sufficiently representative of actinide solid/liquid partitioning for performance assessment modeling of actinide transport in the Culebra formation. Revision of these ranges is not suggested on the basis of the evaluations described here. EPA understands that the effects of organic ligands could be better ascertained through the conduct of K_d experiments under pH, $\text{CO}_2(\text{g})$, and solution compositions comparable to those expected for the repository, but EPA also believes that ranges used are justified and are sufficiently conservative for use in PA.

4.2 COMPARISON OF DOE K_d VALUES WITH OTHER SOURCES

The actinide K_d s described by Brush (1996a, 1996b) were determined for brine solutions with dolomite rock from the Culebra member for a range of $\text{CO}_2(\text{g})$ partial pressures. The brines used in the experimental studies include Brine A, which represents the Salado formation water, ERDA6 which represents the Castile formation water, and AISinR and H-17, which both represent the Culebra formation water (Brush, 1996a; Brush, 1996b). The conduct of K_d experiments in these different solutions produced a range of K_d values for each actinide. To provide a context for the ranges in actinide K_d s, EPA compared these to values reported for a range of geologic media commonly used in environmental studies (Table 4).

In most cases, EPA found that the actinide K_d s determined for the WIPP brines fall into the lower range of values reported for sands, loams, and clayey soils with the possible exception of Np(IV) (Table 1). Sheppard and Thibault (1990) report a lower range of K_d s for Np than Brush (1996a, 1996b) but they did not indicate an oxidation state, making a direct comparison impractical. The K_d range for Np(V) reported by Brush (1996a, 1996b) is comparable to that reported by Sheppard and Thibault (1990).

EPA believes that less retention of the actinides in brine solutions compared to dilute solutions would be expected because of saturation of available adsorption sites by the high concentrations of ionic species present in the brines. This process would reduce the number of sites available for the adsorption of actinide ions. Additionally, the dolomite rock would probably be expected to have less sorptive capacity than the oxides, clays, and organic material commonly present in soils, resulting in proportionately lower K_d s. Oxides, oxyhydroxides, and organic matter are generally thought to be the primary sorbents in most soils, although carbonates are also known to affect metal solute mobilities by providing surfaces for adsorption and nucleation reactions (McLean and Bledsoe, 1992).

Previous work by Dosch and Lynch (1980) on radionuclide adsorption to Culebra dolomite also provides a few values for comparison. These workers report K_d s for Pu and Am of 7,000 and 20,000, respectively, but did not indicate oxidation states. These K_d s are at the high end of the ranges reported by DOE (Table 4).

The previous work by Dosch and Lynch (1980) with Culebra dolomite also indicated

that a single K_d value did not accurately represent solute retention in their experiments. To account for variabilities in K_d s caused by heterogeneities in brines and sorbents, DOE's approach is to use a range and distribution of K_d values so that the uncertainties in any single value are taken into consideration. EPA believes this approach is appropriate.

4.3 ASSESSMENT OF K_d DISTRIBUTION

Brush (1996a, 1996b) recommends the use of a uniform distribution about an arithmetic average to represent the range of K_d values for the actinides, based on the observation that the measured minima and maxima are 3 orders of magnitude or less apart. EPA notes that this approach differs from observations of K_d distributions in the literature. Previous reviews have found that K_d s for numerous metal solutes in different media, mostly different types of soils, are lognormally distributed (Sheppard and Thibault, 1990; and Sheppard et al., 1984; Sheppard and Evenden, 1989, cited by Sheppard and Thibault, 1990). The ranges of K_d s reported by Sheppard and Thibault (1990) vary over four orders of magnitude for many metals, probably because of large differences in the adsorption capacities of the different materials used in the studies included in their review.

The experimental measurements of K_d s described by Brush (1996a, 1996b) were focused on only one type of material, the Culebra dolomite rock, hence these measurements might be expected to show uniform distributions in arithmetic space. However, the experiments were conducted for four different brine compositions and a range of $\text{CO}_2(\text{g})$ partial pressures. These factors introduce variability in the results almost as great as those observed for different soils by Sheppard and Thibault (1990).

EPA observes that there different methods exist for testing the normality of data. One method is simply to make visual examinations of histogram plots of the frequency of occurrence of data. For example, a plot of the frequency of occurrence of the measured K_d s for Pu(V) (from Tables B-1 to B-4 in Brush, 1996a; Brush, 1996b), does not show a uniform distribution over the arithmetic range of determination (Figure 1a). If the K_d s are log-transformed and replotted, then the frequency of occurrence shows a more uniform distribution (Figure 1b). This observation suggests that the measured K_d s for the actinides from Brush (1996a, 1996b) have a loguniform distribution.

According to EPA guidance (EPA, 1992), a standard method for determining normality of data is to construct probability diagrams in which one axis is scaled to represent probabilities according to a normal distribution and the data are arranged in ascending order. If the data are normal, then the points plotted in such a manner will approximate a line. Significant curvature in the data deviating from a linear trend indicates that the data are not normally distributed.

Probability plots were constructed for the actinide K_d s to test for normal distributions on arithmetic and logarithmic scales. The data examined included all of the qualified K_d s reported for brines from the Los Alamos National Laboratory Empirical Sorption Study by Triay as reported by Brush (1996a, 1996b).

A probability plot for the Pu(V) K_d s shows considerable curvature when plotted on an arithmetic scale (Figure 2a) but the data approximate a line when plotted on a logarithmic scale (Figure 2b). This test indicates that the Pu- K_d s have a loguniform distribution. The K_d s measured for Pu(V) were used to represent Am(III) and Pu(III) because of the failure of the Am(III) experiments. Thus, EPA concluded that a log-transformed distribution would provide a better representation of the K_d distributions for Am(III) and Pu(III) than a uniform distribution about an arithmetic average.

The same test was applied to the K_d data for Th(IV), Np(V), and U(VI) and produced the same result as obtained for Pu(V), that is, the log-transformed K_d s show normal distributions whereas their arithmetic equivalents do not (Figures 3, 4, and 5). The probability plot for the U(VI) K_d s also suggests a separate population of data with low K_d values as indicated by the deviation from the linear trend at low percent probabilities (Figure 5).

EPA concludes that these analyses indicate the actinide K_d s are loguniformly distributed and would be better represented by sampling from a log-transformed range rather than the arithmetic uniform range advocated by Brush (1996a, 1996b). A loguniform distribution for K_d s is also consistent with previous reviews of metal partitioning (Sheppard and Thibault, 1990). This finding is important because it means that the median values of the actinide K_d s input to the performance assessment will be consistent with the most commonly determined values in the experiments, rather than skewed by inclusion of a few very high values. For example, the K_d s determined for Pu(V) under various conditions range from 10 to 7,540 ml/g. The arithmetic mean of these two values is 3,775 ml/g. However, the mean of the log-transformed minimum and maximum K_d s is 275 ml/g ($10^{2.44}$), which is a better representation of the median of the experimental data (Figure 1).

4.4 FIELD VERSUS LABORATORY DERIVED K_d VALUES

One of the key considerations in the development of scientifically sound data for use in the CCA calculations is whether field experimental data are required to for adequate characterization of actinide K_d s. K_d values determined experimentally can be scale dependent. That is, small scale experimental studies may not yield the same results as large scale studies. Furthermore, K_d s are site-specific parameters because they incorporate the characteristics of the solute, solution and the solid media into a single parameter to describe partitioning. Ideally, a field experiment that incorporated all of the characteristics likely to occur under repository conditions would provide a more representative assessment of actinide K_d s. However, EPA concludes that this is highly impractical for a number of reasons including:

- ◆ the large scale of the transport pathway in both length and time (over several kilometers and travel times on the order of tens of thousands of years) actual actinides;
- ◆ the hazardous characteristics of the solute (the actinides themselves) precludes meaningful performance of field tests during an experimental program of even dozens of

years; and

- ◆ the lack of experimental control on the physical system could make interpretation of data difficult in that adsorption phenomena could not be differentiated from other chemical and physical processes.

K_d data could be collected from scaled down field experiments that are designed to isolate some particular process or effect. But even scaled-down field experiments encounter many of the same problems previously described for a full-scale experiment.

Due to the practical limitations of field K_d experiments, laboratory experiments are typically conducted. Laboratory experiments are a more efficient use of resources if a wide variety of conditions must be considered. Laboratory experiments tend to be more easily designed to provide bounding or conservative values for a specific process than field experiments.

Also, EPA concludes that because K_d values used in mathematical models cover reasonable ranges for the parameters of interest and the ranges are conservatively broad enough to include minimum K_d s, the issue of field versus laboratory data becomes less important (noting that the PA model is a reasonable representation of the conditions of the site).

In DOE's computer modeling, DOE has identified that K_d s as low as 1-3 ml/g are adequate to achieve compliance (Letter from G. Dials to R. Neill, A-93-02, II-D-115). EPA's modeling of the effects of chemical retardation also indicate that low K_d values (6-20 ml/g) are sufficient to significantly retard actinides in the WIPP disposal system (Docket, A-93-02, V-B-7). Follow up column tests of K_d s show that the minimum K_d values for Am, Pu and Th are at least 100 ml/g (Letter from G. Dials to R. Neill, A-93-02, II-D-115). EPA concludes that the combination of computer modeling and experimental work conducted by DOE are adequate for use in performance assessment without conducting field sorbing tracer tests.

5.0 MODEL APPLICATION AND EFFECTS OF K_d ON ACTINIDE TRANSPORT

5.1 MODEL APPLICATION OF K_d

The WIPP CCA included results of a performance assessment (PA) in which Complementary Cumulative Distribution Function (CCDF) curves for the normalized cumulative radionuclide release(s) to the accessible environment were computed. A component of this assessment included the simulation of groundwater flow and radionuclide transport in the Culebra Dolomite member of the Rustler Formation.

Actinide transport in the Culebra was simulated using the codes SECOFL2D and SECOTP2D (Ramsey, 1996). SECOFL2D is a two-dimensional groundwater flow model capable of simulating transient and steady state flow in porous media (WPO#37271). SECOTP2D is a two-dimensional dual porosity transport model capable of simulating transport of radionuclides through fractured porous media (WPO#36695). Parallel plate type fracturing is assumed in the SECOTP2D code. Fluid flow is restricted to the advective continuum (fractures) and mass is transferred between the advective and diffusive continuum (matrix) via molecular diffusion. The SECOTP2D model is capable of simulating retardation of actinides in both the advective and diffusive continuum using linear equilibrium sorption isotherms. However, sorption was restricted to the matrix in the simulations. No credit was taken for actinide sorption in the advective porosity (along fracture linings) (Brush, 1996a, 1996b).

DOE's initial step in the flow and transport analysis was to generate the Culebra transmissivity field. One hundred equally likely representations of the transmissivity field were generated using geostatistical analysis to quantify the uncertainty associated with that component of the analysis. The one hundred transmissivity fields each reproduced the observed steady state and transient state heads at the Culebra boreholes and honored the measured transmissivity data (Lavenue, 1996).

The PA analysis was based on two sets of transmissivity fields, one with mining restricted to areas outside the Land Withdrawal Boundary (LWB) (partial mining scenario), and one with all regions mined (the full mining scenario). These two scenarios were used to produce two sets of groundwater flow fields. Mining impacts were incorporated into the analysis by uniformly scaling the transmissivity in areas of potential (mineable) resources by a factor 1 to 1000. Outside the LWB, it was assumed mining would occur prior to sealing the disposal facility. Inside the LWB, mining is assumed to occur with a probability of 1 in 100 each century (Ramsey, 1996).

Flow fields were calculated over a regional and a local scale. The regional simulations were performed to incorporate natural flow boundaries into the problem domain that may influence the direction and magnitude of flow in the region of interest. Results of the regional scale simulations were used to interpolate boundary conditions at the local scale. The boundaries of the local scale model were selected to facilitate the computation of integrated discharges across the LWB (Ramsey, 1996).

The transport simulations were calculated using the only the local flow field (grid). Only dissolved species were considered in the transport simulations and transport of four actinide isotopes with a total of six oxidation states was simulated including ^{241}Am , ^{239}Pu , ^{234}U , and ^{230}Th . A key assumption applied to the transport model was that spatially averaged, constant transport parameters can be used to describe the behavior of a heterogeneous fractured porous medium. However, the transport parameters were varied from one run to the next through sampling to account for the uncertainty due to heterogeneity. An actinide source, representing discharge from an intrusion borehole penetrating the repository, was injected into the Culebra as part of the model. A mass flux rate was specified in the model such that one kg of each isotope was injected over a fifty-year period. The results of the transport simulations predict the movement of radioisotopes for scenarios in which either the partial or full mining scenario is in place for the 10,000-year period. The integrated release of each isotope at the LWB is stored as a function of time and used in the construction of the CCDFs (Ramsey, 1996).

K_d s are not used as direct input into the model, rather, the following procedure is employed. The parameter OXYSTAT is sampled to determine the oxidation state of those actinides that have multiple oxidation states, the actinides (e.g. Pu(III) and U(IV), or Pu(IV) and U(VI)) as described in Section 3.0. After the oxidation state has been designated, then the K_d range for the appropriate actinide oxidation states are sampled based on the selected probability distribution. Once the K_d s have been sampled, they are converted into retardation coefficients. The retardation coefficients are then translated (along with other relevant transport and radionuclide parameters) using a preprocessor into the input files used in SECOTP2D. SECOTP2D then solves a system of coupled, linear transport equations, which are then converted (using a post-processor) into formats that can be used to generate CCDFs (Ramsey, 1996).

5.2 RESULTS OF DOE CCA PA

Groundwater flow and radionuclide transport were simulated by DOE in the PA to compute the cumulative release of radionuclides through the Culebra to the accessible environment. Results of the model simulations indicate that the release of radioisotopes from an intrusion borehole to the accessible environment in 10,000 years via transport through the Culebra is improbable (A-93-02, II-G-1, CCA Chapter 6.5).

Three replicates were conducted by DOE for both the full and partial mining scenario to achieve confidence in the results. A replicate consists of 100 model runs for each mining scenario with distinct combinations of input parameters. To complete all three replicates, a total of 600 flow simulations and 600 transport simulation with five independent species were run (^{230}Th the daughter product of ^{234}U was distinguished and simulated independently of the ^{230}Th introduced in the source term) (Ramsey, 1996).

In the first two replicates, no runs resulted in a release at the LWB that exceeded 10^{-30} kg in 10,000 years. Only two runs of replicate three had a combination of input parameters that resulted in a non-zero release at the LWB. The partial mining and full mining runs with this

particular combination occurred twice in the 600 parameter sample sets, indicating a low probability of occurrence. DOE concluded that using Culebra transport does not have significant impact on the final CCDF for total releases using calculations uniform distributions for K_d s (A-93-02, II-G-1, CCA Chapter 6.5).

In addition to the PA transport model used in the CCA, DOE performed bounding estimates using the minimum K_d s necessary to achieve compliance with EPA limits (Marietta and Larson, 1997). The bounding estimates were made for ^{239}Pu and ^{241}Am , which are considered the critical actinides with respect to releases to the accessible environment. Results of DOE's bounding assumptions (whereby all other factors are set to the least favorable value) indicate that a K_d of 3 ml/g is sufficient for compliance for ^{239}Pu and ^{241}Am . Estimates based on typical CCA sample sets indicate that K_d s greater than 1 ml/g are sufficient for compliance (Marietta and Larson, 1997). The K_d ranges determined from DOE experiments and literature for ^{239}Pu and ^{241}Am are typically greater than 100 ml/g, thus inferring that K_d values used in PA are more than sufficient to ensure compliance with EPA limits with respect to accessible environment release through the Culebra.

5.3 RESULTS OF THE PA VERIFICATION TEST

The EPA required DOE to perform verification testing of the DOE PA analyses supporting the WIPP CCA using alternative parameter values (refer to EPA's Technical Support Document: Parameter Justification Report, 1997, A-93-02, V-B-14, for discussion of PAVT parameters). The PA verification test (PAVT) results from PAVT replicate 1 were provided by DOE to EPA (A-93-02, II-G-26). Although the PAVT incorporates verification of all components of the PA, this report addresses PAVT results of the simulations that involve SECOTO2D, as this is the PA code in which K_d s are used to simulate the retardation of actinide transport in the Culebra.

The primary difference in the use of K_d s between the PAVT and the CCA was that K_d s were represented in the PAVT using a log-uniform distribution rather than a uniform distribution (DOE, 1997). The same range of K_d values used in the CCA for each probability distribution were also used in the PAVT. Additionally, there were several significant code changes made to SECOT2D subsequent to the CCA calculations. These changes were documented in Change Control Form, WPO #45730. The code changes were made to improve the computational efficiency and accuracy of the code. Refer to EPA's Technical Support Document for Section 194.23 (A-93-02, V-B-6) for additional discussion of the SECO code modifications.

The use of a log-uniform instead of a uniform distribution resulted in lower K_d values being sampled in the PAVT. This resulted in a greater number of realizations where ^{234}U was discharged across the LWB. In the CCA, only two realizations resulted in conditional releases across the LWB. In the PAVT, 42 realizations produced conditional releases of ^{234}U across the LWB in excess of 10^{-10} kg. Of these, 15 realizations produced a conditional release greater than

0.1 kg. (This assumes that the amount injected into the Culebra is 1.0 kg).³ All of the conditional releases greater than 10^{-10} kg had a sampled value for OXYSTAT that exceeded 0.5, corresponding to a ^{234}U oxidation state of (VI) which has the lower range for the K_d .

Although releases through the Culebra across the LWB were higher in the PAVT than the CCA (because of greater proportion of sampled low K_d values), the cumulative releases from the Culebra under the PAVT were still insignificant relative to the total releases (PAVT results, DOE, 1997). The total PAVT releases were dominated by cuttings and spillings releases with a smaller contribution from direct brine release. Table 5 lists the releases from each of the individual release mechanisms. The long-term releases from the Culebra are zero for the 0.1 probability of release for both the PAVT and CCA. The long-term release from the Culebra is zero for the 0.001 probability of release for the CCA and only 0.0007 for the PAVT. For more discussion on this table see the Technical Support Document: Overview of Major Performance Assessment Issues (A-93-02, V-B-3).

The PAVT mean CCDF for total normalized releases to the accessible environment still did not exceed or come within an order of magnitude of the EPA Limit. EPA concludes that although releases to the accessible environment through the Culebra appear to be highly sensitive to K_d s, total releases to the accessible environment are relatively insensitive to the results of the Culebra flow and transport model.

5.4 RESULTS OF ADDITIONAL EPA MODELING

Additional modeling was performed by the EPA (Docket, A-93-02, V-B-7) to evaluate the effect of K_d groundwater flow and transport in the Culebra. Low-end K_d values were simulated for U ($3.0 \times 10^{-5} \text{ m}^3/\text{kg}$) and Am and Pu ($0.02 \text{ m}^3/\text{kg}$) using the transport code STAFF3D and the mean transmissivity field from the 1992 PA. Radioactive decay of the solute was not simulated. Assuming a network of 10 fractures, breakthrough occurs at the downgradient edge of the land withdrawal boundary at about 3,000 years for uranium. Breakthrough does not occur at relative concentrations greater than 1×10^{-5} during the 10,000 year simulation for Am or Pu. For a scenario in which 100 fractures are simulated, no breakthrough is observed at relative concentrations greater than 1×10^{-5} during the 10,000 year simulation for U, Am or Pu. The results of these model simulations are in reasonable agreement with the results of the CCA and the PAVT. These results support the conclusions previously stated that releases across the LWB through the Culebra are relatively insignificant compared to total releases from all mechanisms.

³In the CCA modeling, DOE assumed that a unit release of 1 kg mass of an actinide was injected into the Culebra. DOE modeled the transport of this unit mass through the Culebra. For the fraction of the 1kg that reaches the boundary, DOE multiplied the fraction by the actinide that is injected to the Culebra via the BRAGFLO calculations.

6.0 CONCLUSIONS

EPA concludes that DOE's experiments provide reasonable actinide K_d values that are appropriate for use in PA. Also, EPA concludes that DOE methodologies regarding oxidation state analogies and distributions, as well as the brine compositions used in PA and application of K_d s in PA, are reasonable. Further, EPA concludes that the values and ranges of actinide K_d s used by the DOE in the PA are reasonable for use in modeling actinide transport in the Culebra. The following conclusions are drawn by DOE and are shared by EPA. These conclusions support retaining the ranges of actinide K_d s advocated by Brush (1996a, 1996b) (Table 3):

- ◆ Under the alkaline conditions expected for the repository, K_d s would generally be expected to be higher than those determined for the near-neutral pHs of the brines used in experimental studies because the cationic nature of the soluble actinide species. Therefore the K_d s used in the CCA PA could be conservative.
- ◆ The K_d ranges for the actinides are generally at the lower spectrum of K_d ranges reported in the literature for actinide retention by various geologic media. Again this could add conservatism to values used by DOE.
- ◆ Concentrations of organic ligands should be highest in the repository and should decrease with distance through mixing with ambient solutions in the Culebra formation, thereby minimizing their potential for affecting actinide K_d s in down-gradient areas.

Also, EPA believes that the effects of organic ligands on actinide K_d s and relevance to transport in the Culebra formation were not completely defined by DOE's experimental studies. However, EPA believes that complexation of organics ligands by divalent cations (Mg^{+2} and Ca^{+2}) and metals (Al^{+3} , Fe^{+2} , Ni^{+2} , Pb^{+2} , *etc.*) may minimize the effects of organics on actinide aqueous speciation and K_d s under expected repository conditions.

EPA also concludes that K_d values derived from DOE experiments appear to be loguniformly distributed, contrary to the DOE position that a linear uniform distribution is appropriate. A loguniform distribution is consistent with trends reported in the literature for retention of solutes by various geologic media. Representation of the actinide K_d s as a loguniform distribution in the PAVT resulted in significant increase in the number of simulations in which releases occurred at the LWB.

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Tables

Table 1. Ranges of matrix K_d s (ml/g) for actinides recommended by Brush (1996b) and used in PA. Values in parenthesis are the revised K_d values recommended in Brush, 1996a, but were not available in time for use in PA.

Oxidation State	Am	Pu	U	Th	Np
III	20-500 (20-400)	20-500 (20-400)			
IV			900-20,000 (700-10,000)	900-20,000 (700-10,000)	900-20,000 (700-10,000)
V					1-200
VI			0.03-30 (0.03-20)		

Table 2. Solution composition used in FMT runs to examine actinide aqueous speciation in the presence of organic ligands.

	ERDA6 Brine	ERDA6 Brine at Equilibrium ^a
Hydrogen	1.112E-02	1.113E+02
Oxygen	5.651E+01	5.653E+01
Sodium	5.499E+00	6.169E+00
Potassium	1.065E-01	1.065E-01
Magnesium	2.087E-02	4.398E-02
Calcium	1.318E-02	1.356E-02
Chlorine	5.272E+00	5.969E+00
Sulfur	1.867E-01	1.871E-01
Carbon	1.757E-02	7.909E-04
Boron	6.919E-02	6.919E-02
Bromine	1.208E-02	1.208E-02
Acetate	1.060E-03	1.060E-03
Citrate	4.650E-04	4.650E-04
EDTA	4.160E-06	4.160E-06
Thorium(IV)	4.699E-08	4.699E-08
Am(III)	1.442E-08	1.442E-08
Np(V)	5.499E-07	5.499E-07

a - Halite, anhydrite, brucite, hydromagnesite [$\text{Mg}_5(\text{CO}_3)_4(\text{OH})_24\text{H}_2\text{O}$]

Table 3. Aqueous speciation of actinides calculated with FMT for the solution compositions given in Table 2.

	ERDA6 Brine (% Total Dissolved)	ERDA6 Brine at Equilibrium ^a (% Total Dissolved)
AmEDTA	97.1	87.4
AmCit ⁰	2.9	1.1
AmAc ⁺²	<0.1	<0.1
ΣAm(III)-hydrolysis	<0.1	9.3
ΣAm(III)-carbonates	<0.1	2.2
ThCit ⁺	85.1	<0.1
ThEDTA ⁰	14.9	<0.1
ThAc ⁺³	<0.1	<0.1
ΣTh(IV)-hydrolysis	<0.1	2.3
ΣTh(IV)-carbonates	<0.1	97.7
ΣTh(IV)-sulfates	<0.1	<0.1
NpO ₂ Ac ⁰	2.2	0.3
NpO ₂ Cit ⁻²	1.9	0.1
NpO ₂ EDTA ⁻³	<0.1	<0.1
ΣNp(V)-hydrolysis	72.9	10.3
ΣNp(V)-carbonates	23.0	89.3

a - Halite, anhydrite, brucite, hydromagnesite [Mg₅(CO₃)₄(OH)₂4H₂O]

Table 4. Actinide K_d s (ml/g) determined for Culebra dolomites under brine conditions compared to those measured for general soil types from Sheppard and Thibault (1990).

Element	DOE K_d	Sand K_d		Loam K_d		Clay K_d	
		Mean ^a	Range	Mean ^a	Range	Mean ^a	Range
Am(III)	20-500	1,900	8.2-300,000	9,600	400-48,309	8,400	25-400,000
Pu(III)	20-500	550 ^b	27-36,000 ^b	1,200 ^b	100-5,933 ^b	5,100 ^b	316-190,000 ^b
Pu(IV)	900-20,000	550 ^b	27-36,000 ^b	1,200 ^b	100-5,933 ^b	5,100 ^b	316-190,000 ^b
U(IV)	900-20,000	ND	ND	ND	ND	ND	ND
U(VI)	0.03-30	35 ^c	0.03-2200 ^c	15 ^c	0.2-4,500 ^c	1,600 ^c	46-395,100 ^c
Th(IV)	900-20,000	3,200	207-150,000	ND	ND	5,800	244-160,000
Np(IV)	900-20,000	5 ^d	0.5-390 ^d	25 ^d	1.3-79 ^d	55 ^d	0.4-2,575 ^d
Np(V)	1-200	5 ^d	0.5-390 ^d	25 ^d	1.3-79 ^d	55 ^d	0.4-2,575 ^d

a - Geometric mean

b - Oxidation state not specified by Sheppard and Thibault (1990); equivalent values assumed for both Pu(III) and Pu(IV).

c - Oxidation state not specified by Sheppard and Thibault (1990); assumed to be representative of U(VI) because of insolubility of U(IV) phases.

d - Oxidation state not specified by Sheppard and Thibault (1990); equivalent values assumed for both Np(IV) and Np(V).

Table 5. CCA and PAVT Normalized Releases for Probabilities of 0.1 and 0.001

Release Mechanism	EPA Units Released @ 0.1 Probability ^a		EPA Units Released @ 0.001 Probability ^a	
	PAVT	CCA	PAVT	CCA
Cutting & Cavings	0.0732	0.0326	0.2754	0.1451
Spallings	0.0756	0.0310	0.2149	0.1750
Direct Brine Release	0.0003	0	0.1545	0.0452
Long-term Brine Release in the Culebra	0	0	0.0007	0
Total	0.1297	0.0576	0.3818	0.2219

a - Releases of 10^{-6} or less are considered to be zero.

Figures