COLLOID-FACILITATED TRANSPORT IN THE SATURATED ZONE: PROCESS-LEVEL SENSITIVITY ANALYSIS

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ABSTRACT

The potential effects of mineral colloids on transport of strongly sorbing radionuclides have long been recognized and studied in laboratory experiments, but field-scale process and model sensitivities have received relatively little attention. New process models for colloid-assisted transport of radionuclides are used in this report to assess the possible effects of natural colloids on the barrier capabilities of the saturated zone at the potential repository at Yucca Mountain, Nevada. The process model includes advection, dispersion, and matrix diffusion of dissolved radionuclides combined with advection and dispersion of radionuclides bound to mobile colloids. Kinetically controlled transfers between the aqueous and colloid-bound state are considered, and the colloids themselves are assumed to exist in mobile, temporarily immobilized, or permanently immobilized states. Plutonium-239 is considered as a representative radionuclide. The effects of uncertainties in the better constrained transport parameters are addressed by Monte Carlo simulation; parameters specific to colloid-facilitated transport are treated as sensitivity parameters and varied across a wide range.
Colloid-facilitated transport is shown to be the dominant transport mechanism for plutonium in both the fractured tuff and alluvium segments of the saturated zone transport path. Transport is strongly dependent on the rate of desorption from colloids and on the rate of permanent filtration of colloids. For nearly irreversible sorption and no filtration, the saturated zone attenuates the plutonium discharge by roughly a factor of 10 in 10,000 years. For nearly reversible sorption, the attenuation is approximately 7 orders of magnitude in 10,000 years. Indications from previously published laboratory experiments on plutonium desorption from colloids, combined with the new modeling results presented here, suggest that plutonium sorption on the majority of colloid sorption sites could be treated as an equilibrium process at the time scales of interest. However, natural colloid populations are clearly heterogeneous and may be governed by multiple rates; irreversible binding of radionuclides to a small fraction of colloids cannot be ruled out.

CONTENTS

Section Page

ABSTRACT iii
FIGURES vii
TABLES ix
ACKNOWLEDGMENTS xi

1 INTRODUCTION 1-1

1.1 Background 1-1
1.2 Risk Significance 1-1
1.3 Objectives 1-2
1.4 Scope 1-2

2 TRANSPORT MODEL 2-1

2.1 Transport Scenario 2-1
2.2 Transport Processes 2-1
2.3 One-Dimensional Radionuclide Transport Equations 2-3
2.3.1 Transport Equations for the Alluvial Aquifer 2-6
2.3.2 Transport Equations for the Tuff Aquifer 2-6

3 GENERIC MODEL AND PARAMETER SENSITIVITIES 3-1

4 MODEL PARAMETERS FOR COLLOID-FACILITATED TRANSPORT 4-1

4.1 Radionuclide Transport Parameters 4-1
4.2 Colloid Transport Parameters 4-1
4.3 Parameters for Radionuclide Sorption onto Colloids 4-2

5 POTENTIAL EFFECTS OF COLLOIDS ON SATURATED ZONE BARRIER PERFORMANCE 5-1

5.1 Fractured Tuff Aquifer 5-1
5.2 Alluvial Aquifer 5-1
5.3 Saturated Zone 5-1

6 DISCUSSION 6-1

7 CONCLUSIONS 7-1

8 REFERENCES 8-1

FIGURES

Figure Page

2-1 Sketch of the Solution-Colloid-Porous Matrix Exchanges Considered in this Report 2-2

3-1 Generic Example Showing Dependence of Normalized Steady-State Radionuclide Breakthrough on Residence Time 3-2
3-2 Same as Figure 2-1, but for Large Sorption Capacity 3-3
3-3 Normalized Steady-State Breakthrough Versus Colloid Retardation Factor for Three Values of Traveltime 3-4
3-4 Normalized Breakthrough Versus Colloid Filtration Rate for Different Values of the Reversibility Ratio *a* 3-4
4-1 Traveltime Distributions Computed Using Algorithms Identical to Those in TPA Version 5.0. 4-3
4-2 Distributions of Colloid Retardation Factors R_c Used by DOE 4-3

5-1 Normalized Breakthrough at the Tuff-Alluvium Interface for Different Values of the Reversibility Ratio *a* 5-2
5-2 Normalized Breakthrough for the Alluvial Aquifer Considered in Isolation for Different Values of the Reversibility Ratio *a* 5-2
5-3 Normalized Breakthrough for the Entire Saturated Zone for Different Values of the Reversibility Ratio *a* 5-3
5-4 Same as in Figure 5-3, but With a Colloid Irreversible Filtration Rate 5-4

6-1 Qualitative Depiction of Critical Region 6-3

TABLES

Table Page

4-1 Reference Case Parameters 4-2

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QUALITY OF DATA, ANALYSES, AND CODE DEVELOPMENT

DATA: No CNWRA-generated original data are contained in this report.

ANALYSES AND CODES: The analyses in this report are documented according to CNWRA quality assurance procedures in Scientific Notebook SN318E.

The commercial software Mathematica™ was used in the process modeling. Software input and output are archived in Scientific Notebook SN318E.

1 INTRODUCTION

1.1 Background

Radionuclides that sorb strongly to minerals in the subsurface also tend to have strong affinity for the naturally occurring mineral colloids that are present in small concentrations within groundwater. In the absence of colloids, strongly sorbing radionuclides are relatively immobile. Once attached to colloids, however, the radionuclides have reduced interactions with the porous medium and may move relatively unretarded through the subsurface. Indeed, colloids have long been recognized as a potentially important factor in enhancing radionuclide migration in the subsurface (Buddemeir and Hunt, 1988; McCarthy and Zachara, 1989; Penrose, et al., 1990). Of particular interest is the fact that colloid-bound plutonium at the Nevada Test Site appears to have traveled hundreds of meters in less than 30 years (Kersting, et al., 1999).

The U.S. Department of Energy (DOE) has taken steps to include colloid-facilitated transport in performance assessment calculations for the potential high-level waste repository at Yucca Mountain, Nevada (Bechtel SAIC Company, LLC, 2003a,b). Multidimensional process modeling and a limited number of experiments (Lu, et al., 1998, 2000) have been undertaken to support the abstraction, which presumes either irreversible attachment to colloids or equilibrium partitioning among the colloid-bound, aqueous, and sorbed states. Similar abstractions are being prepared by the CNWRA for the TPA Version 5.0 code.

Although several studies have compared colloid-facilitated transport models with experiments at the column scale (Saiers and Hornberger, 1996; van de Weerd and Leijnse, 1997; Lührmann and Noseck, 1998; Noell, et al., 1998), understanding of colloid-facilitated transport at the field scale is less developed. In particular, the most significant parameters controlling field-scale transport, and even which processes need to be included in a field-scale model, remain to be fully defined. Cvetkovic, et al. (2004) made a preliminary assessment of parameter and model sensitivities for field-scale, colloid-facilitated transport in the saturated zone. That study identified kinetic effects (in particular, the kinetics of radionuclide desorption) and colloid filtration as key processes. However, the Cvetkovic, et al. (2004) study did not consider matrix-diffusion effects. Thus, its application to the fractured tuff segment of the transport path at Yucca Mountain is limited. Moreover, the focus was on transport under steady-state conditions without consideration of transient effects. Such a steady-state analysis is useful as a first step for understanding parameter and model sensitivities but cannot accommodate a finite compliance period.

This report extends the previous work of Cvetkovic, et al. (2004) to include transient solutions, the effects of matrix diffusion, and probabilistic analyses considering key parameter uncertainties. Both the fractured tuff and alluvial segments of the saturated zone transport pathway are considered. The broad objective is to assess potential effects of colloid-facilitated transport on the barrier capabilities of the saturated zone, with particular emphasis on understanding sensitivities to model parameters and modeling approaches.

1.2 Risk Significance

The Risk Insights Baseline Report (NRC, 2004) concludes that colloid-facilitated transport in the saturated zone is of medium significance to waste isolation based on the potential for colloids to

enhance transport of the strongly sorbing actinides americium and plutonium. These two elements comprise 98 percent of the radiological inventory, based on activity, at 1,000 years (NRC, 2004). Performance effects of colloid-facilitated transport have not yet been assessed with the TPA Version 5.0 code, but an earlier version of the TPA code was used to bound the effects by assigning no retardation to americium, plutonium, and thorium. That conservative analysis increased dose at 10,000 years by nearly two orders of magnitude in comparison to the basecase. In addition, sorption in the alluvium—a process potentially affected by the presence of colloids—was concluded to be of high significance to waste isolation. The Risk Insights Baseline Report also recognizes that colloid transport in the geosphere is subject to significant uncertainties and recommends that additional analyses be undertaken to identify more realistic approaches for colloid-facilitated transport.

DOE analyses have also identified colloid-facilitated transport as a potentially important contributor to dose. In the total system performance assessment–site recommendation, colloidal plutonium is the second highest contributor to dose after 70,000 years (CRWMS M&O, 2000).

1.3 Objectives

The broad objective is to assess potential effects of colloid-facilitated transport on the barrier capabilities of the saturated zone. The specific objectives are

(I) Develop more realistic process models that can be used in confirmatory analyses and in support of total-system performance assessment model abstractions

(ii) Identify key processes and parameters affecting colloid-facilitated transport in the saturated zone

(iii) Assess the potential for colloids to degrade saturated zone barrier performance

1.4 Scope

The potential for naturally occurring colloids to enhance transport in the saturated zone is addressed in this report. Transport in the unsaturated zone and engineered barriers is not considered, nor is the effect of anthropogenic colloids produced from degradation of the wasteform or engineered barriers. The focus is on performance of the fractured tuff and alluvial aquifers as transport barriers. Plutonium-239 is used as a representative radionuclide. An idealized release scenario involving a constant rate of release initiated at $t = 0$ is considered, and normalized breakthrough of plutonium for the time period $t = 0$ to 10,000 years is monitored. The effects of uncertainties in key transport parameters are included through Monte Carlo simulations.

2 TRANSPORT MODEL

2.1 Transport Scenario

The transport scenario considered here is identical to that used in the TPA code (Mohanty, et al., 2002) for the saturated zone. Specifically, transport is conceptualized as occurring in one dimension along a streamtube or flow path that starts in the saturated zone directly below the repository and travels through the fractured tuff and alluvial aquifers to pumping locations south of the repository. The TPA code central streamtube is considered. The flow rate in the central streamtube is fixed at 252 m^3/day [8,890 ft^3/day] per meter of aquifer thickness. The width of the streamtube varies along the streamtube trajectory, which results in a spatially variable velocity. Travel distance is fixed at 18 km [11.2 mi], but the proportion of the flow path in the tuff and alluvium is uncertain because of uncertainty in the position of the tuff and alluvium contact. Uncertainties in the tuff and alluvium porosities introduce additional uncertainties in the total traveltime along the path.

2.2 Transport Processes

The radionuclide transport processes represented here include those represented in the TPA code. In addition, key processes controlling colloid behavior and colloid-facilitated transport of radionuclides are represented in detail.

Within the streamtube, radionuclides in solution are advected by the moving water and are also subject to longitudinal dispersion. Within the alluvium, downstream movement is slowed by equilibrium sorption on the mineral grains. Within the tuff segment of the path, sorption occurs only in the matrix. Radionuclides must diffuse from the fractures to the matrix before they can access the sorption sites. This diffusive mass transfer is modeled as a first-order kinetic process (mobile-immobile model).

The groundwater is assumed to contain naturally occurring colloids. Colloids are advected with the flowing water and are subject to longitudinal dispersion. Downstream movement of colloids is slowed by reversible sorption, which is modeled as an equilibrium process. Colloids may also be permanently removed as a result of physical filtration processes. Colloid concentration is assumed to be constant in time and space, implying that colloid filtration is balanced by colloid generation.

Radionuclides may attach to colloids, thereby facilitating radionuclide transport. Radionuclide attachment to colloids is modeled as a kinetic process with forward (sorption) and reverse (desorption) rates. Because the colloids themselves may exist in up to three states (mobile, temporarily immobilized or sorbed, and permanently immobilized or filtered), mass exchanges between solution and several colloid-bound states are considered. These various exchanges, along with associated rate constants, are shown in Figure 2-1. By proper specification of the various rate constants, the kinetic model includes the entire range of sorption behaviors. Irreversible sorption is obtained by setting reverse rates to zero, while equilibrium sorption is obtained by letting the forward and reverse rates go to infinity.

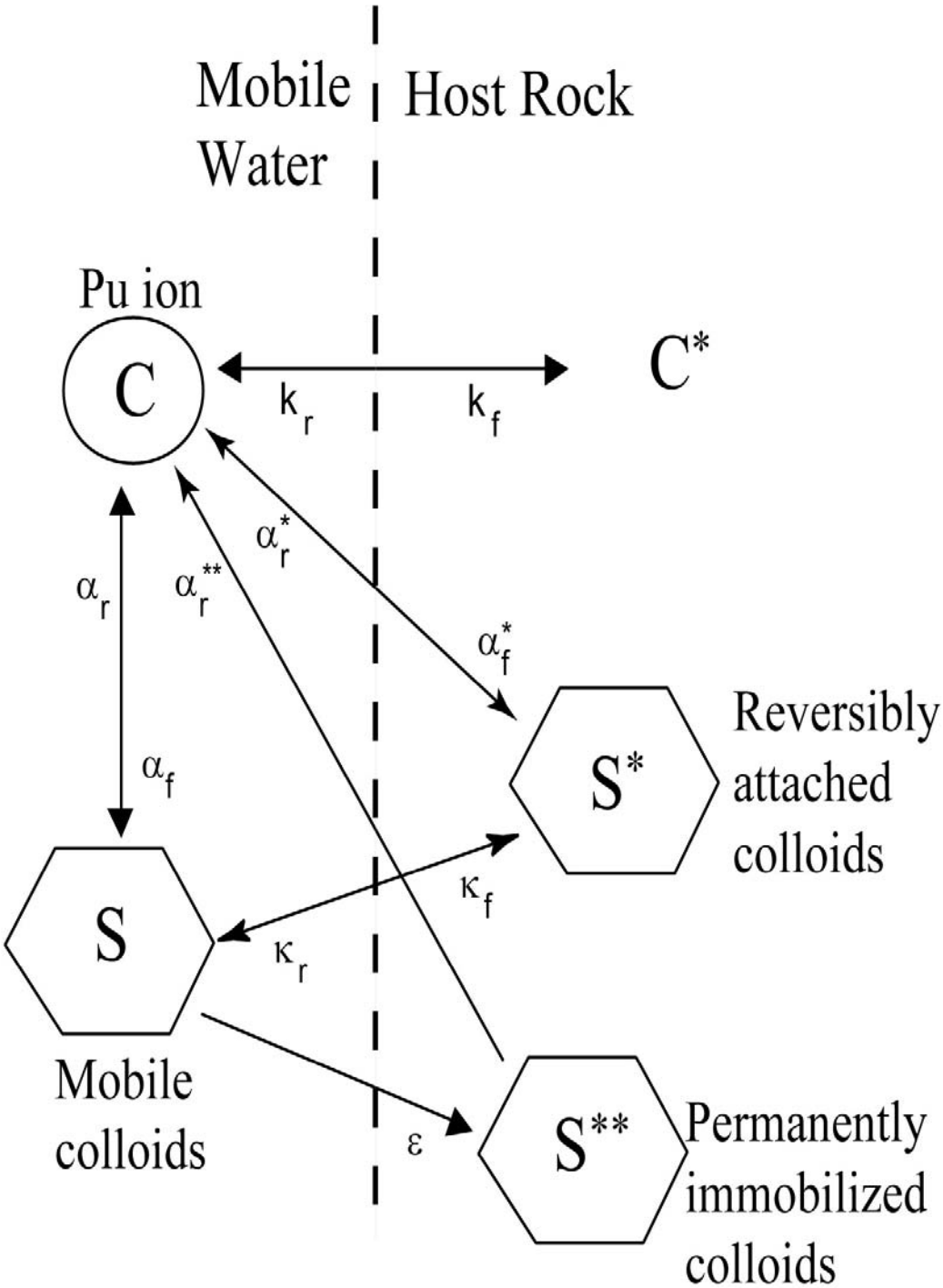

Figure 2-1. Sketch of the Solution-Colloid-Porous Matrix Exchanges Considered in this Report

2.3 One-Dimensional Radionuclide Transport Equations

The conservation equations for radionuclides can be expressed mathematically as

$$\frac{\partial C}{\partial t} + \mathcal{J}C = -\psi^{C\to S}(C,S) - \psi^{C\to S^*}(C,S^*) - \psi^{C\to S^{**}}(C,S^{**}) - \psi^{C\to C^*}(C,C^*) - \lambda C \quad \text{(2-1a)}$$

$$\frac{\partial S}{\partial t} + \mathcal{J}S = \psi^{C\to S}(C,S) - \psi^{S\to S^*}(S,S^*) - \psi^{S\to S^{**}}(S,S^{**}) - \lambda S \quad \text{(2-1b)}$$

$$\frac{\partial C^*}{\partial t} = \psi^{C\to C^*}(C,C^*) - \lambda C^* \quad \text{(2-1c)}$$

$$\frac{\partial S^*}{\partial t} = \psi^{S\to S^*}(S,S^*) + \psi^{C\to S^*}(C,S^*) - \lambda S^* \quad \text{(2-1d)}$$

$$\frac{\partial S^{**}}{\partial t} = \psi^{S\to S^{**}}(S,S^{**}) + \psi^{C\to S^{**}}(C,S^{**}) - \lambda S^{**} \quad \text{(2-1e)}$$

where C is the concentration of radionuclides in solution, C^* is the concentration of immobile radionuclides, S is the concentration of radionuclides attached to mobile colloids, S^* is the concentration of radionuclides attached to temporarily immobilized colloids, and S^{**} is the concentration of radionuclides attached to permanently immobilized colloids. All concentrations are defined on a bulk aquifer volume basis. The ψ terms represent the various exchanges. The differential operator $\mathcal{J}$ is the transport operator representing advection and dispersion processes.

Taking into account that the temporarily immobilized colloids attach and detach quickly from the porous matrix and can be modeled with an equilibrium model $S^* = K_c S$, the transport equations become

$$\frac{\partial C}{\partial t} + \mathcal{J}C = -\psi^{C\to S}(C,S) - \psi^{C\to S^*}(C,K_C S) - \psi^{C\to S^{**}}(C,S^{**}) - \psi^{C\to C^*}(C,C^*) - \lambda C \quad \text{(2-2a)}$$

$$R_C\frac{\partial S}{\partial t} + \mathcal{J}S = \psi^{C\to S}(C,S) + \psi^{C\to S^*}(C,K_C S) - \psi^{S\to S^{**}}(S,S^{**}) - \lambda R_C S \quad \text{(2-2b)}$$

$$\frac{\partial C^*}{\partial t} = \psi^{C\to C^*}(C,C^*) - \lambda C^* \quad \text{(2-2c)}$$

$$\frac{\partial S^{**}}{\partial t} = \psi^{S\to S^{**}}\left(S,S^{**}\right) + \psi^{C\to S^{**}}\left(C,S^{**}\right) - \lambda S^{**} \tag{2-2d}$$

where K_c is the dimensionless distribution coefficient for colloids on porous matrix and $R_c = K_c^{-1}$ is the colloid retardation factor.

The various exchange terms in Eqs. (2-2a through 2-2d) can be linear or nonlinear, equilibrium or kinetically controlled. Linear models are generally applicable when the sorption capacity is large relative to the local aqueous concentration. Cvetkovic, et al. (2004) evaluated linear and nonlinear models for sorption on colloids, and they concluded that conditions expected in the Yucca Mountain saturated zone are well within the range of validity for linear models. Assuming linear exchanges,

$$\psi^{C\to C^*}\left(C,C^*\right) = k_f C - k_r C^* \tag{2-3a}$$

$$\psi^{C\to S}\left(C,S\right) = \alpha_f C - \alpha_r S \tag{2-3b}$$

$$\psi^{C\to S^*}\left(C,S^*\right) = \alpha_f^* C - \alpha_r^* S^* \tag{2-3c}$$

$$\psi^{C\to S^{**}}\left(C,S^{**}\right) = -\alpha_r^{**} S^{**} \tag{2-3d}$$

$$\psi^{S\to S^{**}}\left(S,S^{**}\right) = \varepsilon S \tag{2-3e}$$

The rates for the exchanges are indicated in Figure 2-1. The α are rates for exchange between solution and colloids, the *k* are rates for exchange between solution and the porous matrix, the α* are rates for exchange between solution and temporarily immobilized colloids , and α** are rates for exchange between solution and permanently immobilized colloids. The subscripts *r* and *f* denote forward and reverse. All these exchanges are bidirectional except for the last two, which are unidirectional (irreversible). The $S\to S^{**}$ exchange is unidirectional by definition because it applies to permanent removal. No forward rate is included in the $C\to S^{**}$ exchange because a permanently removed colloid is indistinguishable from the porous matrix, and that exchange is presumably already counted in the measured rates for $C\to C^*$ exchange.

Two additional assumptions help simplify the set of exchanges. First, the rate coefficients for desorption from colloids are assumed to be identical irrespective of whether the colloid is mobile or immobile. Thus, $\alpha_r = \alpha_r^* = \alpha_r^{**}$. Second, the forward rate for sorption on colloids should be proportional to the concentration of sorption sites, and thus proportional to colloid concentration. This assumption implies $\alpha_f^* = K_C \alpha_f$.

The transport model then becomes

$$\frac{\partial C}{\partial t} + \mathcal{J}C = -k_f C + k_r C^* - \alpha_f R_C\ C + \alpha_r R_C\ S + \alpha_r S^{**} - \lambda C \tag{2-4a}$$

$$R_C \frac{\partial S}{\partial t} + \mathcal{J} S = \alpha_f R_C C - \alpha_r R_C S - \varepsilon S - \lambda R_C S \tag{2-4b}$$

$$\frac{\partial C^*}{\partial t} = k_f C - k_r C^* - \lambda C^* \tag{2-4c}$$

$$\frac{\partial S^{**}}{\partial t} = \varepsilon S - \alpha_r S^{**} - \lambda S^{**} \tag{2-4d}$$

The differential operator $\mathcal{J}$ in Eqs. (2-4a through 2-4b) represents the transport processes. In the familiar Eulerian form, the operator is

$$\mathcal{J} = v \frac{\partial}{\partial x} - D \frac{\partial^2}{\partial x^2} \tag{2-5}$$

where $D = a|v|$ is the longitudinal dispersion coefficient, v is velocity, a is the dispersivity, and x is position along the streamtube. Writing the dispersivity as a fixed fraction f of the travel distance L, the transport operator becomes

$$\mathcal{J} = v \frac{\partial}{\partial x} - f\, L\, |v| \frac{\partial^2}{\partial x^2} \tag{2-6}$$

Note that both v and L are uncertain. Uncertainty in L comes from uncertainty in the tuff-alluvium contact, while uncertainty in v comes from uncertainty in porosity and possibly total flow rate in the streamtube. These two uncertain parameters can be collapsed to a single uncertain parameter by re-writing the transport operator in a Lagrangian form. Switching independent variables from position x to traveltime $\tau = x/v$, yields the Lagrangian form of the transport operator

$$\mathcal{J} = \frac{\partial}{\partial \tau} - f\, \tau_L \frac{\partial^2}{\partial \tau^2} \tag{2-7}$$

where $\tau_L = L/v$ is the global traveltime. With this form of the transport operator, the concentrations are functions of τ and time, and uncertainties in travel distance and velocity are manifest through the uncertainty in the total traveltime $\tau_L = L/v$.

The system Eqs. (2-4a through 2-4d) with the transport operator Eq. (2-7) is the general model used for this study. With appropriate choice of the various exchanges, it represents the transport effects of equilibrium, slowly reversible, or irreversible sorption to colloids for the tuff and alluvial aquifers. For example, if the $C \rightarrow C^*$ exchange is modeled as a fast exchange then the radionuclide sorption (on the matrix) becomes the equilibrium model. If the $C \rightarrow C^*$ exchange is modeled with a first-order kinetic model, then the mobile-immobile model used to represent matrix diffusion can be recovered.

2.3.1 Transport Equations for the Alluvial Aquifer

For the alluvial aquifer, the $C \rightarrow C^*$ exchange is assumed to be fast compared to other rates and transport times of the system. This implies, $C^* = K_d'$ where $K_d' = k_f / k_r$ is the dimensionless distribution coefficient. The transport model then becomes

$$R \frac{\partial C}{\partial t} + \mathcal{J} C = -\alpha_f R_C C + \alpha_r R_C S + \alpha_r S^{**} - \lambda R C \tag{2-8a}$$

$$R_C \frac{\partial S}{\partial t} + \mathcal{J} S = \alpha_f R_C C - \alpha_r R_C S - \varepsilon S - \lambda R_C S \tag{2-8b}$$

$$\frac{\partial S^{**}}{\partial t} = \varepsilon S - \alpha_r S^{**} - \lambda S^{**} \tag{2-8c}$$

where $R = 1 + K_d'$ is the retardation factor.

2.3.2 Transport Equations for the Tuff Aquifer

In the fractured tuff part of the flow path, sorption of radionuclides on the fracture surfaces is neglected, consistent with the abstractions in the TPA code (Mohanty, et al., 2002). Radionuclides must first diffuse from the fractures into the matrix before they can access sorption sites. This process can be modeled with a mobile-immobile approximation.

To obtain the mobile-immobile model from Eqs. (2-4a through 2-4d), the immobile concentration is divided into concentration in stagnant water regions and concentration sorbed on the porous matrix. Assuming equilibrium partitioning between the two immobile states, $C^* = R_S C'$, where C' is the radionuclide concentration in immobile water, $R_S = 1 + \frac{1-\theta_{im}}{\theta_{im}} \rho_b K_S$ is the matrix retardation factor, K_s is the distribution coefficient, ρ_b is bulk density, and θ_{im} is the matrix porosity. Defining the forward rate as $k_f = \beta_0 \omega$, and the reverse rate as $k_r = \beta_0 / R_S$, with $\omega = \theta_{im} / \theta_m$ and $\beta_0 = \frac{D}{0.28}\left(\frac{2n}{f}\right)^2$ where D is the diffusion coefficient, n is the number of fractures per unit meter, f is the fraction of the matrix porosity that is participating the diffusion process, the following transport equations are obtained

$$\frac{\partial C}{\partial t} + \mathcal{J} C = -\beta_0 \left(\omega C - C'\right) - \alpha_f R_C C + \alpha_r R_C S + \alpha_r S^{**} - \lambda C \tag{2-9a}$$

$$R_C \frac{\partial S}{\partial t} + \mathcal{J} S = \alpha_f R_C C - \alpha_r R_C S - \varepsilon S - \lambda R_C S \tag{2-9b}$$

$$R_S \frac{\partial C'}{\partial t} = \beta_0 \left(\omega C - C' \right) - \lambda R_S C' \tag{2-9c}$$

$$\frac{\partial S^{**}}{\partial t} = \varepsilon S - \alpha_r S^{**} - \lambda S^{**} \tag{2-9d}$$

In the absence of colloids, these equations are identical to those solved in the flow and transport module within TPA (Mohanty, et al., 2002).

3 GENERIC MODEL AND PARAMETER SENSITIVITIES

Cvetkovic, et al. (2004) explored generic model and parameter sensitivities related to the transport model given in Eqs. (2-4a through 2-4d). They considered a unit step input of plutonium released into the streamtube starting at $t = 0$. Because the focus was on broad-scope sensitivities, they ignored transients and monitored the steady-state discharge as $t \to \infty$. At steady state, the plutonium discharge is smaller in magnitude than the plutonium input at the start of the streamtube because of radionuclide decay. The magnitude of the steady state throughput provides a convenient measure of performance of the saturated zone as a barrier. Sorption on colloids was modeled in a kinetic framework, using the linear, bilinear, and Langmuir sorption models. Sensitivities to the key controlling parameters were identified.

The main conclusions on model and parameter sensitivities are (Cvetkovic, et al., 2004)

(I) Under some conditions, colloid-facilitated transport can enhance the throughput of plutonium by many orders of magnitude, depending on the traveltime, the rate of desorption from colloids, and the sorption capacity (See Figures 3-1 and 3-2).

(ii) Nonlinear models for sorption on colloids generally predict smaller throughput of plutonium, but for typical field conditions, the differences between the linear and nonlinear models are relatively minor; thus, the linear model provides a useful estimate.

(iii) Temporary immobilization (retardation) of colloids is relatively ineffective at reducing the plutonium throughput, unless the retardation factor is large (>100). In fact, the throughput of plutonium depends nonmonotonically on the colloid retardation factor R_c, first rising with increasing R_c and then falling with increasing R_c for large R_c (see Figure 3-3). This nonmonotonic behavior is a consequence of mass exchange between solution and temporarily immobilized colloids. However, this finding of relative insensitivity to colloid retardation is based on an asymptotic analysis $t \to \infty$. Consideration of a finite time window may change these sensitivities.

(iv) Permanent immobilization of colloids is generally more effective at reducing plutonium throughput. However, with permanent immobilization of colloids, the throughput becomes very sensitive to the rate of plutonium desorption from colloids (Figure 3-4). If permanent immobilization is included, then irreversible binding to colloids is not a conservative assumption.

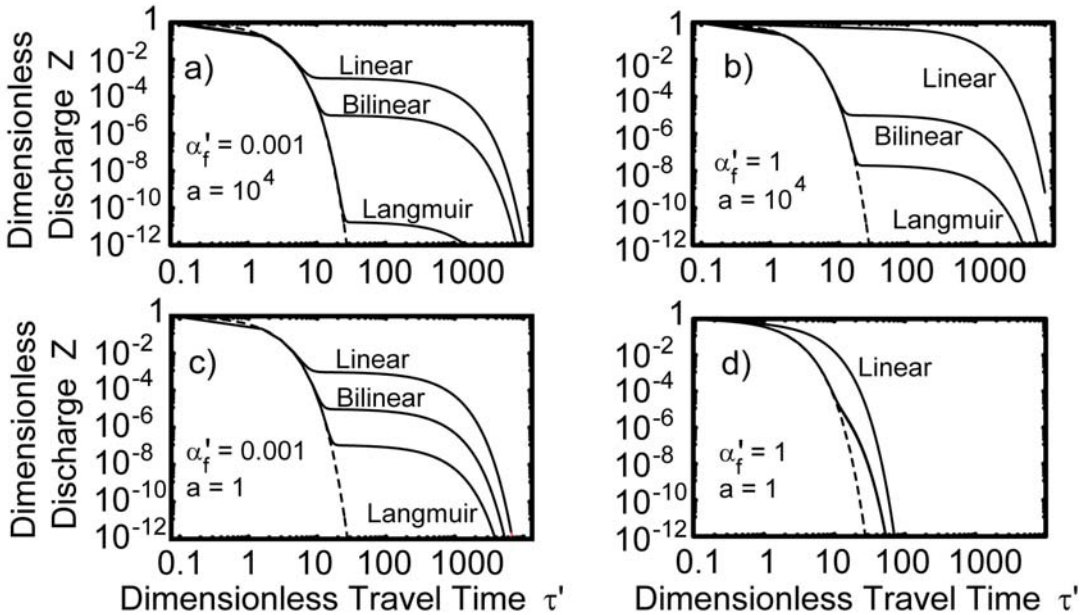

Figure 3-1. Generic Example Showing Dependence of Normalized Steady-State Radionuclide Breakthrough on Residence Time τ' for Linear and Two Nonlinear Sorption Models Assuming a Small Sorption Capacity (Cvetkovic, et al., 2004). The Dimensionless Residence Time Is $\tau' = \tau R \lambda$ Where *R* Is the Retardation Factor, λ Is the Radionuclide Decay Rate, and τ Is the Water Residence Time. Four Combinations of Normalized Forward Rate and Reversibility Factors Are Shown: (a) Slow Forward Rate and Slowly Reversible; (b) fast Forward Rate and Slowly Reversible; (c) Slow Forward Rate and Strongly Reversible, and (d) Fast Forward Rate and Strongly Reversibly. The Case Without Colloids Is Shown as a Dashed Curve.

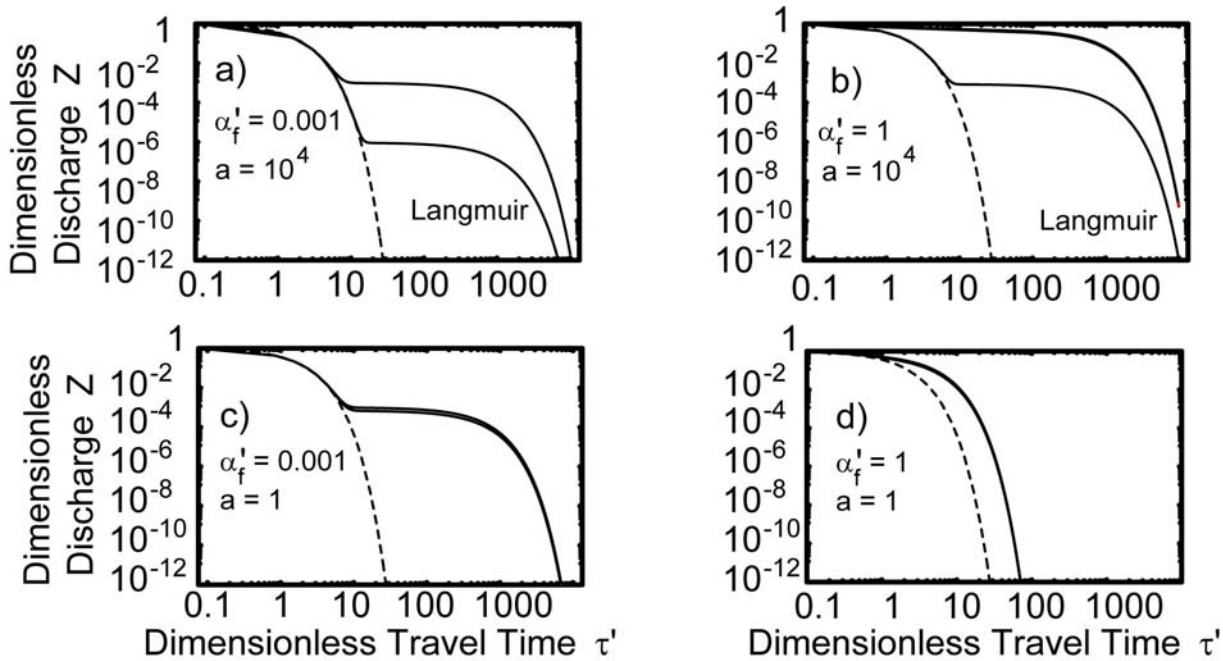

Figure 3-2. Same as Figure 2-1, but for Large Sorption Capacity (Cvetkovic et al., 2004). In the Situation of Large Sorption Capacity, the Linear and Bilinear Models Coincide for the Entire Range of Dimensionless Traveltime and for All Four Combinations of Rate Parameters. In the Strongly Reversible Cases c) and d), the Two Nonlinear Models Coincide with the Linear Model.

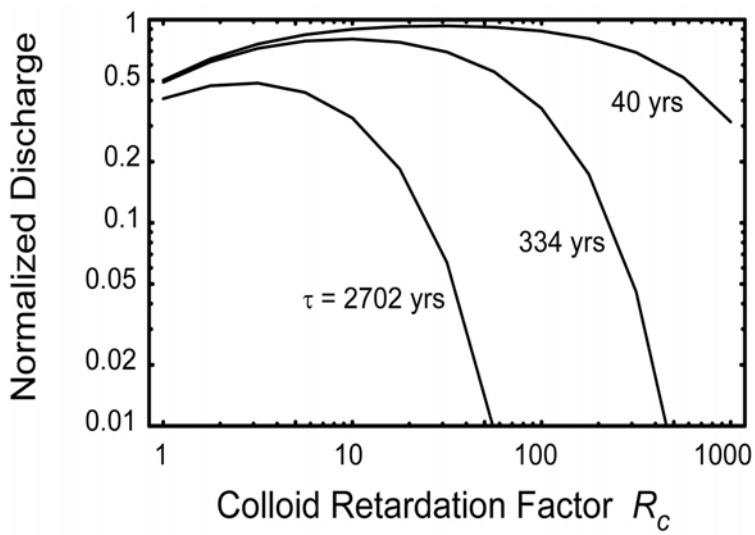

Figure 3-3. Normalized Steady-State Breakthrough Versus Colloid Retardation Factor for Three Values of Traveltime Corresponding to the 99th, 50th, and 1st Percentile (Cvetkovic, et al., 2004). The Reversibility Factor is Fixed at 1,000 in this Example, and There Is No Colloid Filtration.

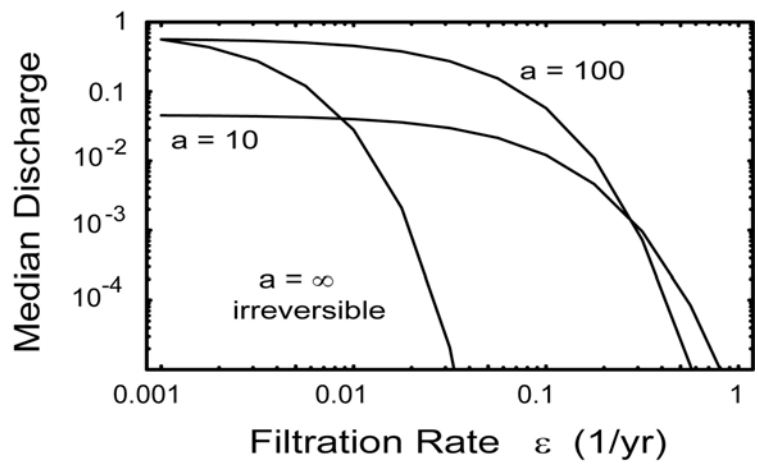

Figure 3-4. Normalized Breakthrough Versus Colloid Filtration Rate for Different Values of the Reversibility Ratio *a*. The Colloid Retardation Factor is 20 in this Example, and the τ = 334 Years.

4 MODEL PARAMETERS FOR COLLOID FACILITATED TRANSPORT

Parameter values and probability distributions required for the analysis were selected to be consistent with the TPA Version 5.0 code basecase input, where possible. Parameter values are summarized in Table 4-1. The technical bases for these parameters are discussed in the following subsections.

4.1 Radionuclide Transport Parameters

The transport of Pu-239 in the form Pu(V) is considered as a representative radionuclide. The relevant radionuclide transport parameters include the groundwater traveltime (τ) distributions for the tuff and alluvium, retardation factors for the fractured tuff and alluvium, and matrix diffusion parameters for the fractured tuff aquifer.

The traveltime distributions were calculated as in the TPA Version 5.0 code. The distance to the tuff-alluvium contact was first sampled, followed by mobile porosity. Using these sampled values and a fixed flow rate in the streamtube, the total traveltime was calculated by integrating velocity along the variable-width streamtube. This calculated traveltime represents one sample from the traveltime distribution. Note that the tuff and alluvium traveltimes are correlated because once the travel distance in the tuff is sampled, the travel distance in the alluvium is then fixed. The resulting traveltime distributions for the central streamtube are shown in Figure 4-1. Only the central streamtube is considered here.

Radionuclide retardation factors in the TPA 5.0 code basecase are not input directly, but are calculated internally based on sampled water chemistry parameters. For this reason, the TPA Version 4.1 code distributions of R_d for plutonium are used for the alluvium. These distributions are similar to the TPA Version 5.0 code distributions. After a R_d value is sampled, the same value is used for the immobile retardation R_s in the tuff matrix. Within the TPA Version 5.0 code, the two retardation factors are perfectly correlated and differ only by a multiplicative factor corresponding to the ratio of specific surface areas. This factor is a relatively minor correction and is ignored.

The matrix diffusion parameters D, f, n, and θ_{im} are identical to those of the TPA Version 5.0 code basecase.

4.2 Colloid Transport Parameters

Colloid transport parameters include colloid retardation in tuff and alluvium, and the irreversible removal rate for colloids ε.

DOE (Bechtel SAIC Company, LLC, 2003b) compiled results from laboratory and field experiments on colloid retardation in alluvial material and in fractured volcanics and used these results to generate probability distributions for use in performance assessment. Some of the retardation factors were calculated from breakthrough curves from short-duration column experiments by numerical parameter estimation. The colloid retardation factors for some of these experiments were nominally estimated to be small; however, the uncertainty in the estimated parameter is so large as to make the estimate indeterminant. For this reason, DOE truncated the distributions at $R_c = 6$ for the tuff and $R_c = 8$ for alluvium (see Figure 4-2).

Table 4-1. Reference Case Parameters			
Parameter	**Distribution**	**Range**	**Source**
Traveltime, τ	Figure 4-1	—	TPA* Version 5.0 code Section 4.1
Radionuclide Retardation Factors, R_d, R_s	Log-normal	4.2×10^2–3.9×10^5	TPA* Version 4.1 TPA* Version 5.0
Immobile Porosity tuff, θ_{im}	Constant	0.2	TPA* Version 5.0
Mobile Porosity tuff, θ_m	Log-uniform	10^{-3}–10^{-2}	TPA* Version 5.0
Matrix Diffusion Penetration Factor, f	Log-uniform	10^{-2}–10^{-1}	TPA* Version 5.0
Diffusion Coefficient, D	Constant	10^{-3}	TPA* Version 5.0
Fracture Spacing, n	Constant	0.05	TPA* Version 5.0
Mobile Porosity Alluvium	Uniform	0.10–0.15	TPA* Version 5.0
Colloid Retardation Factor, R_c	Figure 4-2	—	†
Colloid Filtration Rate, ε	Constant	0	Section 4.2
Forward Rate Constant, α_f	Constant	0.1 yr^{-1}	Section 4.3
Reversibility Ratio $a = \frac{\alpha_f}{\alpha_r}$	Sensitivity Parameter	5 to ∞	Section 4.3

*Mohanty, S., T.J. McCartin, and D.W. Esh. "Total-system Performance Assessment (TPA) Version 4.0 Code: Module Descriptions and User's Guide." San Antonio, Texas: CNWRA. 2002.
†Bechtel SAIC Company, LLC. "Technical Basis Document No. 8: Colloids." Rev. 02. Las Vegas, Nevada: Bechtel SAIC Company, LLC. 2003a.
———. "Saturated Zone Colloid Transport." ANL–NBS–HS–000031. Rev. 01. Las Vegas, Nevada: Bechtel SAIC Company, LLC. 2003b.

The DOE truncated distributions are used here.

In considering permanent removal rates, it is important to make the distinction between naturally occurring colloids and anthropogenic colloids such as corrosion products. The latter are much more likely to be permanently removed as a result of filtration. It is also important to realize that permanent removal means immobilization for transport time scales of interest. For naturally occurring colloids, no evidence exists for colloid immobilization for the time scales of interest (hundreds to thousands of years). For this reason, the conservative assumption of no irreversible colloid filtration is used ($\varepsilon = 0$).

4.3 Parameters for Radionuclide Sorption onto Colloids

The experiments of Lu, et al. (1998, 2000) provide data on the rates for radionuclide sorption and desorption on colloids. They considered Pu-239 and Am-243, with the plutonium being

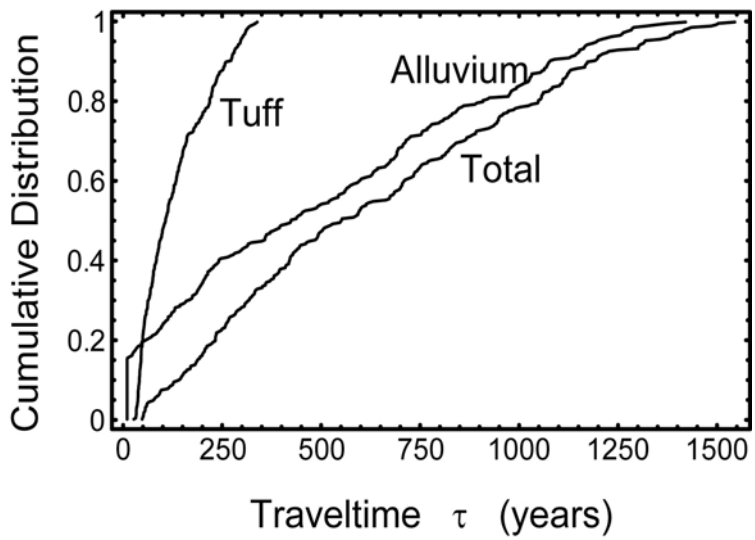

Figure 4-1. Traveltime Distributions Computed Using Algorithms Identical to Those in TPA Version 5.0 Code. Results Are Shown for the Tuff and Alluvial Segments of the TPA Central Streamtube.

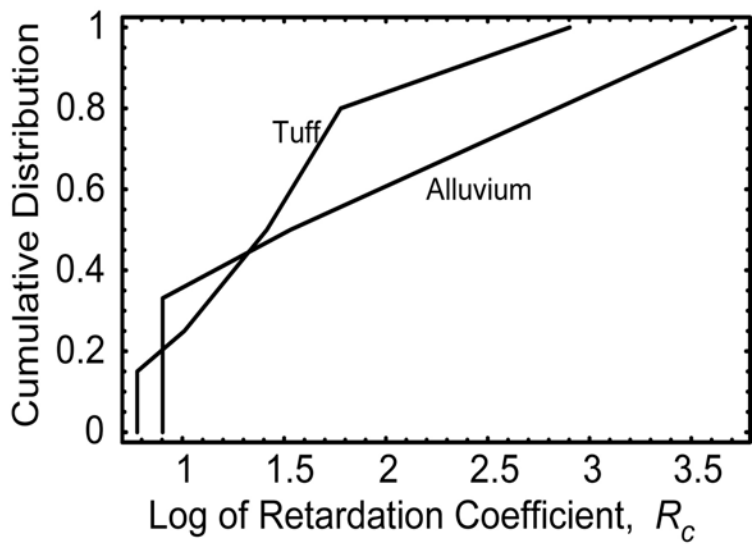

Figure 4-2. Distributions of Colloid Retardation Factors R_c Used by DOE

prepared in both colloidal Pu(IV) and soluble Pu(V) forms. Strong sorption and relatively weak desorption on hematite, goethite, montmorillonite, smectite, and silica colloids were observed. Americium and plutonium sorption showed similar trends and similar magnitudes for the sorption parameters.

Painter, et al. (2002) reanalyzed the Lu, et al. (2000) data. They pointed out that the data clearly show evidence for two forward sorption rates and that the slower rate is the one that is relevant for field-scale applications. Cvetkovic, et al. (2004) assumed a linear relationship between the forward sorption rate and the colloid concentration, and scaled forward rates estimated from the Lu, et al. (2000) data to field-relevant colloid concentrations. They estimate forward sorption rates of approximately 0.1 yr^{-1}. This value is used here.

Lu, et al. (1998, 2000) also performed desorption experiments. In the Lu, et al. (1998) experiments, 1 percent of Pu(V) desorbed from smectite colloids after 150 days. For montmorillonite and silica, the fraction desorbed was approximately 0.5 and 1 percent, respectively. Desorption from hematite and goethite colloids was even slower. In the Lu, et al. (2000) experiments, desorption proceeded at a faster rate, with 17–21 percent of Pu(V) desorbing from montmorillonite and 17–20 percent desorbing from silica colloids in 295 days.

Clearly, desorption rates are slow and highly uncertain. A reversibility ratio is defined in this report as $a = \alpha_f / \alpha_r$ and treated as a sensitivity parameter. Small values of a indicate strongly reversible sorption, and large values indicate weakly reversible. The 0.5 to 1 percent desorbed fraction observed in the 150-day Lu, et al. (1998) experiments implies a desorption rate of 0.01-0.02 yr^{-1}, which corresponds to a reversibility ratio of 5–10. The reversibility factor a is varied in the range 5 to infinity.

5 POTENTIAL EFFECTS OF COLLOIDS ON SATURATED ZONE BARRIER PERFORMANCE

5.1 Fractured Tuff Aquifer

Normalized breakthrough curves at the tuff-alluvium interface are shown in Figure 5-1 for different values of the reversibility ratio *a*. In these simulations, the fractured tuff aquifer is initially free of radionuclides. At the beginning of the simulation, the inlet concentration is set to a nonzero value, which is held constant throughout the simulation. The breakthrough curves are normalized by the inlet concentration and are averages for 300 realizations.

The case *a* = 5 corresponds to a desorption rate of 0.02 yr^{-1}, which is in the range inferred from multistep desorption experiments (Lu, et al., 1998) involving Pu-239(V) sorbed to smectite. Although slow on the time scale of laboratory experiments, such a rate represents relatively reversible attachment of radionuclides to colloids on transport time scales of 10,000 years. For the *a* = 5 situation, the breakthrough is approximately 0.1 percent at 10,000 years; the fractured tuff aquifer has attenuated the radionuclide discharge by a factor of 1,000. In the situation of no colloids, the breakthrough is negligible in 10,000 years because of matrix diffusion and strong plutonium sorption on the tuff matrix. Thus, colloid-facilitated transport is the dominant transport mechanism for plutonium in the fractured tuff aquifer, even for relatively rapid desorption.

The calculated breakthroughs are sensitive to the reversibility ratio (or desorption rate). Increasing *a* to 50 increases the 10,000-year breakthrough to approximately 6 percent. For *a* = 500, the 10,000-year breakthrough is approximately 20 percent and the 20,000-year breakthrough is almost 40 percent. For this combination of input parameters, the situation of *a* = 500 is close to the irreversible limit; increasing *a* beyond 500 results in no significant increase in breakthrough.

5.2 Alluvial Aquifer

Similar results are shown in Figure 5-2 for the alluvial aquifer. For the alluvium, the no-colloids breakthrough is less than 0.1 percent at 10,000 years. With colloids and a reversibility factor of *a* = 5, the 10,000-year breakthrough is increased to nearly 3 percent. Thus, colloid-facilitated transport is also the dominant transport mechanism in the alluvial aquifer. The breakthrough is less sensitive to the reversibility ratio, as compared with tuff aquifer. For nearly irreversible sorption (*a* = 5,000), the breakthrough is about 18 percent at 10,000 years.

5.3 Saturated Zone

Results for the entire saturated zone are shown in Figure 5-3. These simulations also use a step function input into the fractured tuff aquifer. For each realization, the calculated breakthrough at the tuff-alluvium interface is then used as the input for the alluvial aquifer. As in Figures 5-1 and 5-2, the breakthrough curves are mean curves averaged for multiple realizations (150 in this case).

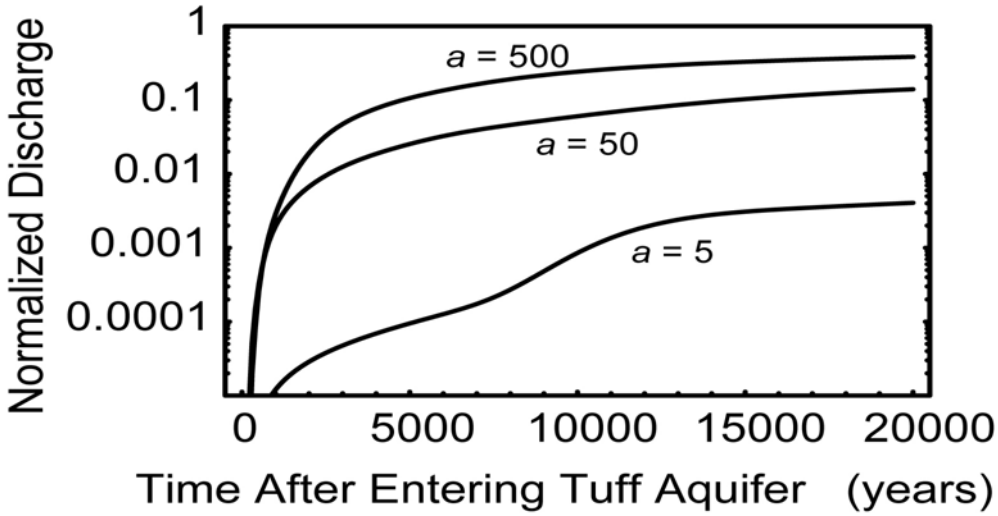

Figure 5-1. Normalized Breakthrough at the Tuff-Alluvium Interface for Different Values of the Reversibility Ratio *a*. The Curves Are Averages of 300 Realizations.

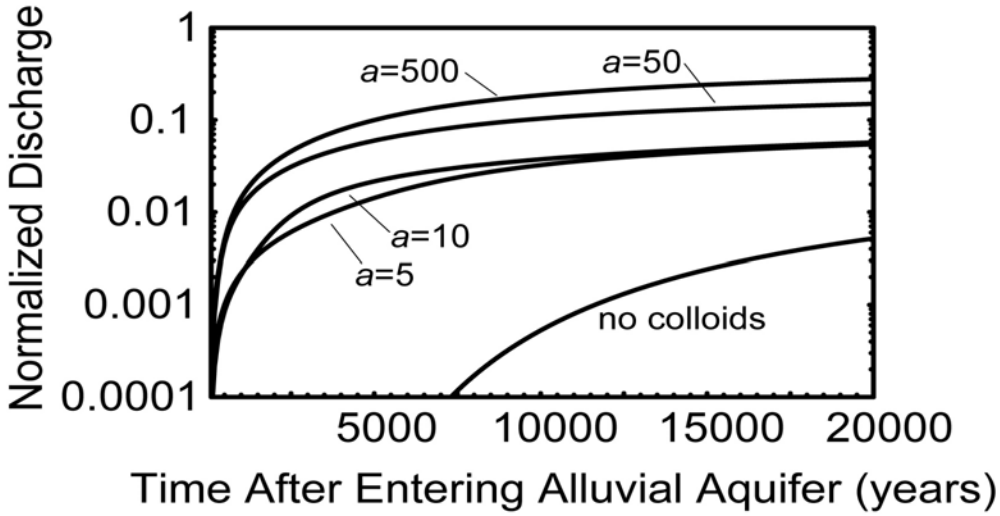

Figure 5-2. Normalized Breakthrough for the Alluvial Aquifer Considered in Isolation for Different Values of the Reversibility Ratio *a*. Also Shown Is the Case Without Colloids. The Curves Are Averages of 300 Realizations.

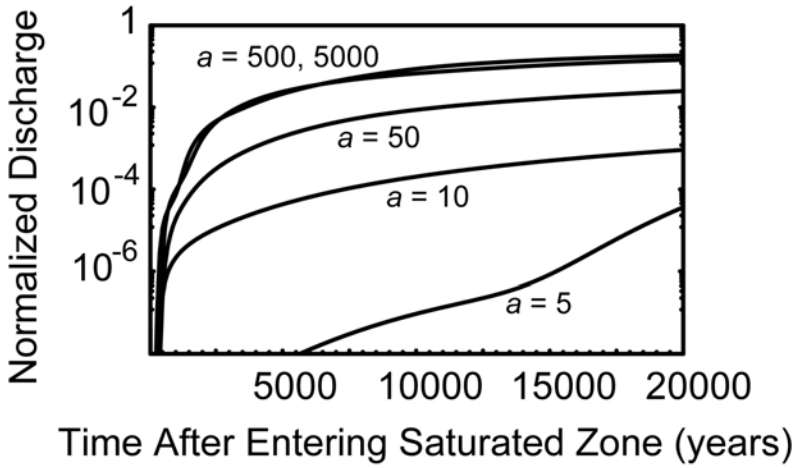

Figure 5-3. Normalized Breakthrough for the Entire Saturated Zone for Different Values of the Reversibility Ratio *a*. For Each Realization, the Breakthrough for the Fractured Tuff Aquifer Is Used as Input Into the Alluvial Aquifer. The Curves Are Averages of 150 Realizations.

For the reversible case with *a* = 5, the 10,000 year breakthrough concentration is about 10^{-7}, indicating that the saturated zone attenuates the radionuclide concentrations by a large amount. For the case *a* = 5,000 (nearly irreversible), the 10,000 year breakthrough is roughly 10 percent.

The 10,000 year breakthrough is similar in magnitude to that calculated by DOE for irreversibly attached colloids. However, the early breakthrough in Figure 5-3 is significantly larger than that the DOE calculations. The differences are caused by differences in the traveltime distributions.

Figure 5-4 shows results for simulations similar to those of Figure 5-3, but with an irreversible filtration rate of 0.05 yr^{-1}. This relatively small value of filtration implies a half-life of approximataely14 years for a mobile colloid. Irreversible filtration reduces the breakthrough for all values of the desorption rate (reversibility ratio), but the effect is most dramatic for the cases of nearly irreversible attachment. The breakthrough becomes relatively insensitive to the reversibility ratio for a > 50 because the attachment to colloids is nearly irreversible on the transport time scale of interest, for those larger values of *a*.

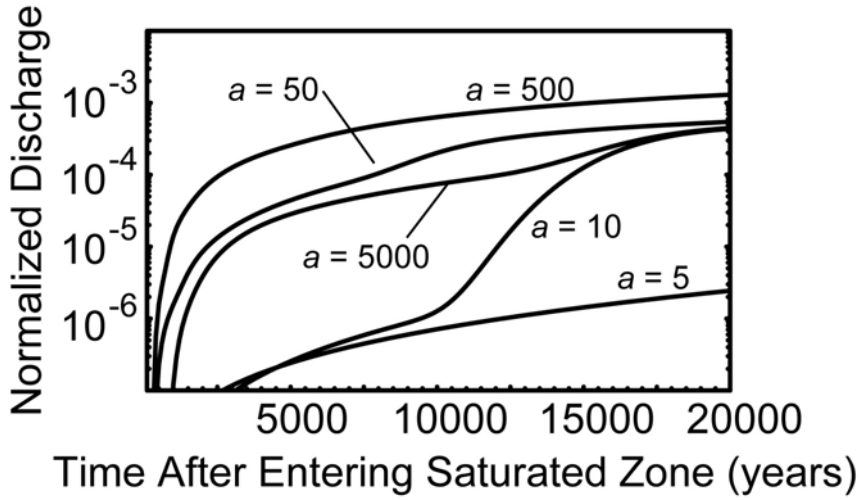

Figure 5-4. Same as in Figure 5-3, But With a Colloid Irreversible Filtration Rate of 0.05 yr^{-1}. Note that the Normalized Breakthrough Does Not Have a Monotonic Dependence on the Desorption Rate (Reversibility Ratio).

6 DISCUSSION

Based on the results presented here and in previous sensitivity studies (Painter, et al., 2002; Cvetkovic, et al., 2004), colloid-facilitated transport is likely to be the dominant transport mechanism in the saturated zone for strongly sorbing radionuclides such as plutonium. The magnitude of the effect is most sensitive to two uncertain parameters: the rate at which colloids are irreversibly filtered from the system, and the rate of radionuclide desorption from colloids. Steady-state transport analyses suggest relative insensitivity to the colloid retardation factor, but these analyses need to be repeated with transient simulations. The colloid retardation factor is better constrained by field and laboratory data, compared with the filtration and description rates.

When considering the irreversible filtration rate, it is important to make the distinction between natural colloids and anthropogenic colloids. The latter are more likely to be permanently filtered, and this filtration is easier to demonstrate in field and laboratory experiments compared with natural colloids. Natural colloids, especially clay or zeolite colloids, are considered to be more relevant for saturated zone transport. Irreversible removal of natural colloids has not been demonstrated in the field, and direct demonstration of colloid immobilization for the transport time scales of interest is unlikely. Moreover, if permanent removal of colloids is assumed, then the breakthrough depends sensitively and nonmonotonically on the rate of radionuclide desorption from colloids. Irreversible attachment to colloids is not a conservative assumption in this situation, and the data requirements for desorption rates would be increased. The DOE is currently not taking credit for permanent removal of natural colloids in the saturated zone, but does use the combination of permanent colloid removal and irreversible attachment to colloids in the unsaturated zone performance abstractions (Bechtel SAIC Company, LLC, 2003a). This permanent removal is meant to represent the expected behavior of colloids generated from the wasteform and from corrosion products and is outside the scope of this report. Consequences of assuming the combination of irreversible attachment and irreversible colloid removal in the unsaturated zone should be analyzed in future studies.

Indirect demonstration of colloid removal may be possible. If natural colloids are being permanently immobilized in aquifers, then this removal must be balanced by colloid generation to maintain the non-zero colloid concentrations ubiquitous in groundwaters. Colloid generation rates measured, for example, by flushing the system with colloid-free water and measuring the colloid concentration in the effluent could be used to infer colloid removal rates, as has been suggested by Kersting and Reimus (2003). Such experiments would need to be conducted for relatively long times (months) to eliminate transient effects of relatively rapidly desorbing colloids.

If the rates of desorption from colloids are on the order of 0.01 yr^{-1} or faster, then the saturated zone appears to be an effective barrier to radionuclide transport after taking into account colloid-facilitated transport. Rates of this magnitude are slow on the time scale of laboratory or field experiments, but are fast relative to the transport time scales of interest. Taken at face value, batch tests of plutonium desorption appear to show rates that are considerably faster than 0.01 yr^{-1} for clays and zeolites; desorption from silica is even faster (Lu, et al., 1998,2000; Kersting, et al., 2003a,b). Moreover, Reimus, et al. (2003) have shown that desorption from colloids in flow-through experiments on fractured cores is considerable faster than in batch experiments. They attribute this difference to collisions between colloids and the fracture surfaces, which allow the fracture surfaces to compete with colloids for radionuclides. However,

these laboratory experiments should be interpreted with caution. The duration of the existing batch experiments is too short to establish whether the desorption can be described by a single-rate desorption model. Indeed, indications are that sorption is best described by multiple sorption rates (Painter, et al., 2002; Reimus, 2003); if multiple sorption rates exist, then the rates inferred from batch experiments may simply be the fastest of several rates. Indeed, irreversible sorption on a fraction of sorption sites cannot be ruled out for the clay and zeolite colloids.

The existing laboratory and field data as well as modeling results on colloid sorption and colloid-facilitated transport can be reconciled by considering that colloids in groundwater exist as heterogeneous populations of several minerals (clays, zeolites, silica, calcite) with a wide range of particle sizes and binding energies for sorption sites. It is reasonable to expect that there would be a range of filtration rates and desorption rates for these heterogeneous populations, which can be represented by a joint probability density function $f(\varepsilon, \alpha_r)$[1]. Clearly the situation of small ε and small α_r produces the largest impact of colloids. Indications are that the bulk of the $f(\varepsilon, \alpha_r)$ distribution probably lies outside the small α_r region, and the small fraction of the $f(\varepsilon, \alpha_r)$ distribution that lies within the critical region is responsible for colloid-facilitated transport observed in the field. This situation is illustrated qualitatively in Figure 6-1. Determination of the fraction of $f(\varepsilon, \alpha_r)$ that is contained in the critical region will require additional field and laboratory tests. Long-term desorption experiments in which plutonium-bearing colloids are repeatedly contacted with plutonium-free water are required to better constrain the desorption rate. From a modeling perspective, a distribution of rate constants and filtration rates would require a multigroup approach in which colloids are partitioned into several groups with different transport and plutonium sorption properties. Nonlinear sorption models with a finite sorption capacity would be required for the nearly irreversible groups to prevent them from gathering all available radionuclides as the simulation progresses. Such a multigroup approach is a conceptually straightforward generalization of the models presented here, but would require additional model and software development.

For that part of the heterogeneous colloid population with rapid desorption rates relative to the transport time scale, equilibrium partitioning of radionuclides among solution, colloids, and porous matrix is an adequate approximation. The effect of those colloids can be modeled using the single-component advection dispersion equation with appropriately defined transport parameters. For the alluvium, colloid-facilitated transport has the net effect of reducing the effective retardation factor. Neglecting colloid filtration and defining a new coefficient K_0 for partitioning between colloids and solution, Eqs. (2-8a through 2-8c) become

$$R^{\text{eff}} \frac{\partial C}{\partial t} + \mathcal{J} C = -\lambda R^{\text{eff}} C \qquad (6\text{-}1)$$

[1]This probability distribution should not be confused with the uncertainty distributions used for performance assessment calculations, which represent lack of knowledge about a single parameter instead of a heterogeneous population governed by multiple rates.

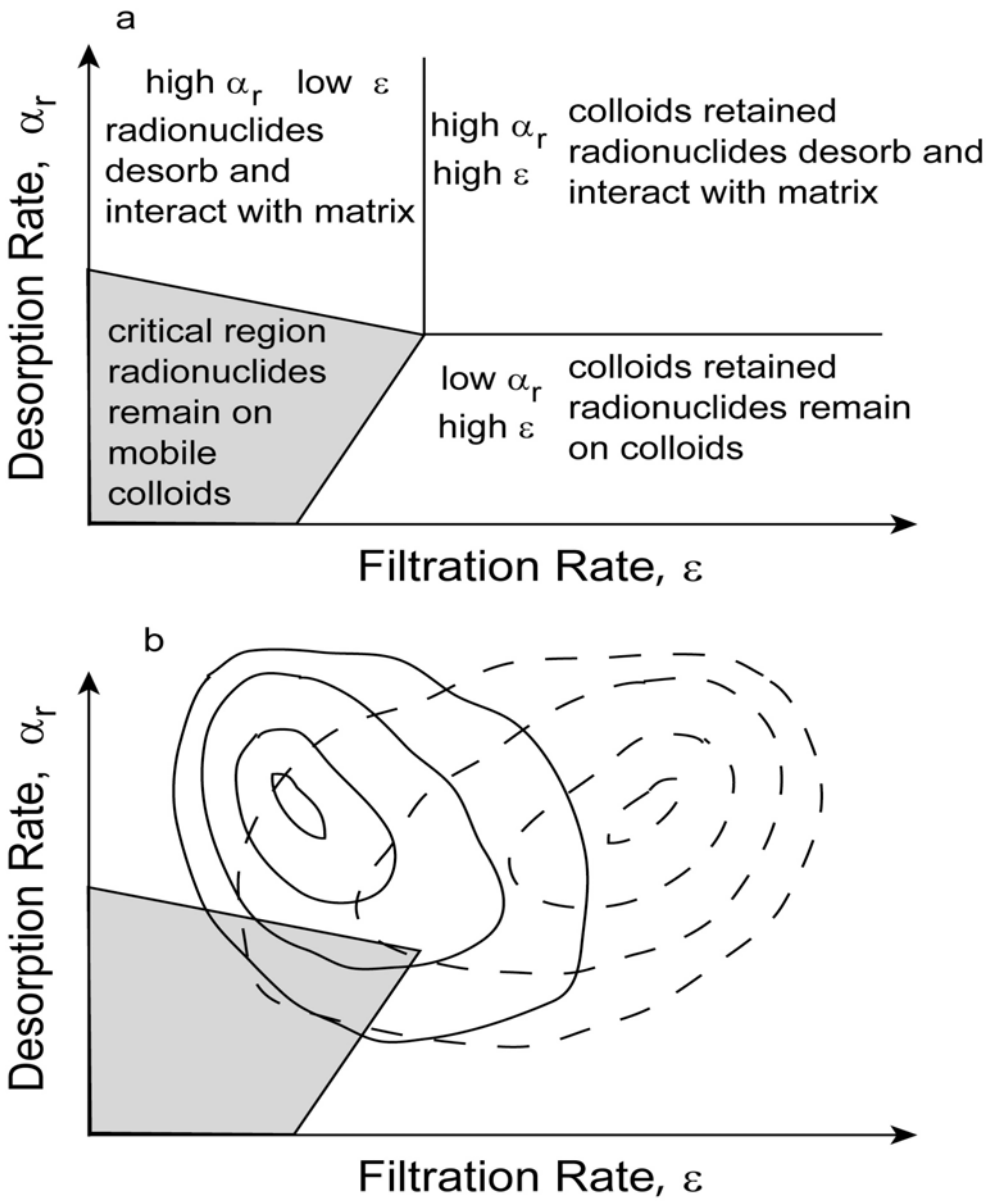

Figure 6-1. Qualitative Depiction of Critical Region of ε, α_r Parameter Space. The Shaded Region With Small ε and α_r Is the Most Critical Area for Transport. The Solid Curves in (b) Represent Contour Levels of a Hypothetical Probability Density for Heterogeneous Population of Colloids Governed by Multiple Rates. The Dashed Curves Represent Another Hypothetical Probability Density With Smaller Filtration Rates. Filtration Rates are Currently Unknown. The (Presumably Small) Fraction of the Population Contained in the Critical Region Is Expected to Be Responsible for Most of the Transport.

where

$$R^{\text{eff}} = \frac{R + K_0 R_c}{1 + K_0} \tag{6-2}$$

is the new effective retardation that takes into account the effects of colloids. Similarly, Eqs. (2-9a through 2-9d) describing transport in the fractured tuff become

$$R_f \frac{\partial C}{\partial t} + \mathcal{L}C = -\beta_0^{\text{eff}}\left(\omega C - C'\right) - \lambda R_f C \tag{6-3a}$$

$$R_S^{\text{eff}} \frac{\partial C'}{\partial t} = \beta_0^{\text{eff}}\left(\omega C - C'\right) - \lambda R_S^{\text{eff}} C' \tag{6-3b}$$

where

$$R_S^{\text{eff}} = \frac{R_S}{1 + K_0} \tag{6-4}$$

$$\beta_0^{\text{eff}} = \frac{\beta_0}{1 + K_0} \tag{6-5}$$

and

$$R_f = \frac{1 + R_c K_0}{1 + K_0} \tag{6-6}$$

Thus, equilibrium partitioning to colloids reduces the mass exchange coefficient and the immobile retardation factor, with the net effect of reducing matrix diffusion. In addition, retardation in the fractures is introduced, with retardation coefficient given by Eq. (6-6). Retardation of radionuclides in the fractures was neglected in Eqs. (2-9a through 2-9d), consistent with the TPA reference case parameter set.

Equation (6-1) is in the form solved in the TPA code. Thus, the effects on transport of rapid attachment and detachment to colloids in the alluvium can already be modeled in the current TPA code by assigning a reduced retardation coefficient according to Eq. (6-2). Equation (6-3) is also in the form solved in the NEFTRAN (Olague, et al., 1991) module of the TPA code. However, the fracture-to-matrix mass transfer coefficient as defined by Eq. (6-5) is element dependent, and an element-dependent mass transfer coefficient is not accommodated in NEFTRAN. Efforts are under way to introduce a species-dependent mass transfer coefficient, which will then allow the effects of equilibrium partitioning to colloids in the fractured tuff to be modeled in future versions of the TPA code.

7 CONCLUSIONS

Based on the results presented here and on information in previously published reports and journal articles, conclusions about colloid-facilitated transport in the saturated zone are as follows.

- Colloid-facilitated transport is likely the dominant saturated zone transport mechanism for strongly sorbing radionuclides like plutonium. Solubility limits may, however, place an upper bound on the total mass that can be transported.

- Colloid-facilitated transport depends most sensitively on two parameters: the desorption rate from colloids and the rate of permanent immobilization of colloids.

- Permanent immobilization of natural colloids is an uncertain process that has not been demonstrated in the field. The conservative assumption of no permanent colloid filtration is probably unavoidable, at present.

- The rate of desorption from colloids is uncertain. Existing desorption experiments suggest that it is slow relative to the time scale of laboratory tests, but fast relative to transport time scales of interest. However, existing laboratory tests cannot rule out irreversible binding to clay or zeolite colloids.

- For plutonium irreversibly bound to colloids, the saturated zone attenuates the plutonium discharge by approximately one order of magnitude.

- If the rates for plutonium desorption from clay colloids measured by Lu, et al. (1998, 2000) are assumed to apply to all sorption sites on all colloids, then radionuclide sorption to colloids is rapid and reversible. In this situation, the saturated zone attenuates the plutonium discharge by approximately seven orders of magnitude.

- In the TPA Version 5.0 code, the effects of equilibrium sorption on colloids are adequately represented for the alluvial aquifer, but not for the fractured tuff aquifer. Modifications to address this limitation are in progress.

- Natural colloids exist as heterogeneous populations that are likely to have a wide range of colloid removal and radionuclide desorption rates acting simultaneously. The existence of multiple rates complicates the interpretation of laboratory and field experiments, as well as modeling. Existing data are insufficient to constrain the joint distribution of rates.

- Conservative (bounding) assumptions concerning colloid-facilitated transport will probably be required in performance assessment calculations, at least in the near term. The models developed in this study provide an additional tool that can be used to help bound the effects of colloid-facilitated transport.

- Additional field and laboratory tests may be able to constrain the distribution of multiple rates in natural colloid populations. New numerical simulation tools that are able to handle multiple classes of colloids with different rates would be needed to interpret such experiments.

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