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MATRIX DIFFUSION SUMMARY REPORT

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ABSTRACT

Matrix diffusion is the migration of dissolved solutes from flowing macropores or fractures into the more-or-less stagnant pores of adjacent rock matrix. This report provides a review of matrix diffusion transport model theory, assumptions, and practical aspects with a goal of assessing the appropriateness of incorporating matrix diffusion into performance assessment (PA) models of the proposed nuclear waste repository at Yucca Mountain (YM), Nevada. Scoping calculations indicate that matrix diffusion model assumptions are reasonable for the low-permeability, fractured tuffs in the saturated zone beneath YM. However, in the unsaturated zone, evidence suggests that diffusive solute transport is either limited or dominated by other transport processes and, as such, the matrix diffusion model is not appropriate for the YM unsaturated zone. Comparisons between first-order kinetic and matrix diffusion solute transport models indicate that first-order kinetic models provide a reasonable approximation of the matrix diffusion process for the cases considered. This last finding is of particular importance because the PA model currently used by the U.S. Nuclear Regulatory Commission already includes a first-order kinetic transport model for radionuclide transport. Future field, laboratory, and modeling investigations are suggested to more accurately constrain matrix diffusion model parameters for PA.

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QUALITY OF DATA, ANALYSES, AND CODE DEVELOPMENT

DATA: No CNWRA original data was generated in this report. Sources for other data should be consulted for determining the level of quality for those data.

ANALYSES AND CODES: A computer code was written to generate the breakthrough curves shown in this report. Although the code is not sufficiently developed to be placed under the CNWRA Configuration Management System, test cases showed that code output is in agreement with published breakthrough curves with the same input parameters.

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1 INTRODUCTION

Yucca Mountain (YM), Nevada is the site of a proposed geologic repository for the disposal of high-level radioactive waste (HLW). Performance assessment (PA) models, which will be used to assess the long-term safety of this candidate repository are being developed by both the U.S. Department of Energy (DOE) and the Nuclear Regulatory Commission (NRC).

It is widely recognized that groundwater transport through both unsaturated and saturated zones is one of the most likely means of radionuclide migration from a geologic HLW repository. As such, improvements to PA models will depend on knowledge of the following issues: (i) rates and patterns of groundwater flow; (ii) maximum concentrations of radionuclides that might be mobilized by water in dissolved form, as colloids, or as particulates; (iii) the sorptive capacity of the rock through which radionuclides might travel; and (iv) the degree to which transport of dissolved radionuclides can be delayed by interaction between flowing macropores and the more-or-less stagnant groundwater that occupies the pore space of adjacent low-permeability matrix (Grisak et al., 1988). The focus of this paper is on issue (iv), often referred to as matrix diffusion which, as this report will show, is inextricably dependent upon the other three issues.

At YM, the process of matrix diffusion may impact repository performance because flow occurs primarily in fractures, which account for only a small fraction of total formation porosity. In such hydrologic systems, matrix diffusion can attenuate migration of radionuclides in two ways: (i) it can spread them physically from the flowing fractures into stagnant pore water, and (ii) rock matrix can provide a vast increase in mineral surface available for geochemical surface reactions (e.g., sorption) as compared to fracture surfaces alone.

Although matrix diffusion has long been recognized as potentially important to repository performance, to date, matrix diffusion has not been abstracted in PA models in ways tied closely to the physics of the system. Several other conceptual models for fracture-matrix interaction have been incorporated into PA codes, however, none of these models are based on known physical processes. Currently, there is no consensus on which conceptual model is most appropriate for the YM hydrologic system.

The purpose of this report is to provide a summary of relevant literature and theory regarding matrix diffusion processes in fractured-rock hydrologic systems. This summary is designed to support the NRC evaluations of conceptual models for matrix diffusion YM PA models. This report includes discussions of the following topics.

- Background: available conceptual models for matrix diffusion and treatment in previous PA codes for YM
- Matrix diffusion transport models: theory, sensitivity, and validity of assumptions
- Matrix diffusion experiments and field testing at YM
- Evidence for limited matrix diffusion
- Needs for further experiments, tests, or modeling

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2 BACKGROUND

2.1 CONCEPTUAL MODELS FOR FRACTURE-MATRIX INTERACTION

Available conceptual models for flow and solute transport in fractured rock include: (i) discrete-feature models; (ii) equivalent continuum-models; (iii) multiple-continuum models; and (iv) hybrid models (Sagar, 1996). Discrete-feature models are those in which individual fractures and matrix blocks are explicitly represented in a numerical grid. This approach is sufficient for small scales where fracture geometry and hydraulic properties are known, and the necessary fine-scale numerical grid does not result in unreasonable computation times. For repository-scale modeling, these models are generally not practical due to lack of knowledge about fracture properties, and excessive computation time. In the equivalent-continuum approach, the bulk properties of the fractured medium are approximated by defining effective properties of a single equivalent continuum based on some observable behavior (e.g., tracer transport) associated with the actual medium. This approach does not explicitly treat the time-dependent interaction of solutes between fractures and matrix. Thus it is only reasonable for modeling single-solute transport at the scale and flow rate on which the equivalent continuum is based. When modeling transport of multiple solutes that may migrate between fractures and matrix at different rates, or when changing flow rates or transport distances result in different time scales for fracture-matrix interaction, equivalent continuum properties must be defined for each solute and for each transport distance and flow rate under consideration. Generally, this is not a practical approach for PA modeling of YM.

Multiple-continuum models treat the composite medium as a superposition of several media of different properties. In the context of fracture-matrix interaction, discussion is limited to dual-continuum models which treat rock matrix and fractures as separate continua that occupy the same computational domain and may or may not be coupled by some type of exchange term. For purposes of this report, dual-continuum models can be divided into two subcategories: dual-permeability models and dual-models. Dual-permeability models allow for advective transport in both rock matrix and fractures. In dual porosity models, it is assumed advective transport occurs only in fractures; water within rock matrix pores is assumed immobile but solutes can transition between the mobile and immobile regions, thus retarding solute migration. Because of the assumed mobile and immobile regions, dual-porosity models are often referred to as "two-region" models (e.g., van Genuchten et al., 1984, van Genuchten 1985). Both dual-permeability and dual-porosity models can be further subdivided according to the method used to couple solute transfer between fracture and matrix continua. These coupling methods may include: no transfer, rate-limited transfer, random transfer, and instantaneous equilibrium.

Hybrid models (e.g., Sagar, 1996) combine some of the properties of both the equivalent-continuum and dual-continuum conceptual models. Each cell in a numerical grid is assigned properties of both fractures and rock matrix. During each time step, solute concentration in a cell is assumed to be in equilibrium between the fracture and matrix. The mass of solute that is exchanged with adjacent cells is the combination of both fracture and matrix components of mass flux, driven by the local hydraulic gradient. Typically much more mass is transported in the fracture component than in the matrix component because of higher fracture permeability. At the end of the time step, the total solute mass in a cell is again assumed to be evenly distributed between fractures and matrix, regardless of whether the majority of solute initially entered the cell through a fracture. This conceptual model is equivalent to a dual-permeability model with instantaneous equilibrium between matrix and fractures, but it is computationally more efficient. A drawback to this type of conceptual model is that there is no clear physical basis for the assumed solute equilibrium between fractures and matrix. It is unclear how well hybrid models can represent cases where the majority of flow occurs in widely spaced preferential flow paths.

All of the above model types have been used to simulate the process of matrix diffusion, and thus can be characterized as matrix diffusion models, even though many have little to do with the physical process of diffusion. Physically based matrix diffusion models are most commonly treated using a dual-porosity approach with rate-limited solute exchange (e.g., Neretnieks, 1980; Tang et al., 1981; Sudicky and Frind, 1986); the rate of transport into or out of the immobile rock matrix is limited by a Fickian diffusion process wherein diffusive flux is proportional to the solute concentration gradient across the fracture-matrix interface. For purposes of this report, the term "matrix diffusion model" refers to this type of dual-porosity model. Another commonly used dual-porosity approach is the first-order-kinetic model (e.g., van Genuchten and Wierenga, 1976) which treats fluid in the immobile region as well-mixed and of uniform concentration; the rate of solute transfer across the fracture-matrix interface is proportional to the concentration difference between the two regions. Although it is seldom the case that water within rock matrix is well-mixed, the first-order-kinetic model is often used to approximate the matrix diffusion model because it has a simpler analytical solution. Both the matrix diffusion model and the first-order-kinetic model are predicated on the assumption that water in the rock matrix pores is immobile. The applicability of this assumption to YM is discussed in section 3.5.1 of this report

2.2 FRACTURE-MATRIX INTERACTION PERFORMANCE ASSESSMENT MODELS

Previous attempts to incorporate fracture-matrix interactions into YM PA models have been based on the dual-permeability approach. For example, the 1995 DOE Total System Performance Assessment (TSPA-1995) (TRW Environmental Safety Systems, Inc., 1995) employed a Markov Transition Model algorithm (Golder Associates, Inc., 1994) to abstract the effects of fracture-matrix interaction during radionuclide transport through the unsaturated zone. This algorithm assumes that radionuclides transition between fracture and matrix after traveling some random distance as determined by a Poisson-process transition rate coefficient. This algorithm predicted significant radionuclide retardation due to fracture-matrix interaction. This method was criticized by the NRC (Codell, 1996) because it assumes rapid transition between fracture and matrix which is inconsistent with the observed lack of chemical equilibrium between fractures and matrix in the unsaturated zone at YM (e.g., Fabryka-Martin et al., 1996; Murphy, 1995).

The NRC Iterative Performance Assessment (IPA), Phase 2 (Nuclear Regulatory Commission, 1995) employed NEFTRAN II (Olague, et al., 1991) to simulate radionuclide transport in saturated and unsaturated zones. Although NEFTRAN II has the capability to model fracture-matrix interaction, this capability was not used for IPA Phase 2. Instead, a preprocessor, FLOWMOD, was used to divide radionuclide transport into fracture and matrix pathways for each hydrogeologic layer. Based on this approach, flow through a single layer can take one of two possible transport paths—fracture or matrix—with the probability of each based on respective permeability. At the end of each layer, the process is repeated for the next layer. In this manner, FLOWMOD calculates average transport velocities for 2^n pathways, where n is the number of layers. This hybrid approach allows interaction between fracture and matrix, and it accounts for the different travel times and fluxes in fracture and matrix. However, there is no physical basis for the resulting fracture-matrix interaction.

Both the NRC and DOE are investigating alternative methods for including the effects of matrix diffusion in their PA codes. For example, at recent technical exchanges DOE technical staff members have suggested the possibility of calculating an increased effective porosity based on various flow and

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transport properties (e.g., Robinson, 1997; Zyvolski, 1997). Such a method would fall under the category of equivalent-continuum approaches, and would be subject to the limitations previously described in section 2.1. That is, an effective porosity would have to be calculated for each solute and each flow rate and model scale under consideration. Additionally, the effective porosity approach may not provide a good approximation of solute breakthrough behavior at an assumed point of exposure. The effects of effective porosity and matrix diffusion on solute breakthrough are discussed in section 3.3 of this report.

As previously mentioned, the NRC PA model incorporates NEFTRAN II (Olague et al., 1991) which can simulate fracture matrix interaction based on the first-order-kinetic model. NRC staff are currently considering the use of this option in future PA models[1]. A comparison of matrix diffusion and first-order-kinetic models can be found in section 3.4 of this report.

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[1] T. McCartin, 1997, Nuclear Regulatory Commission, personal communication.

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3 MATRIX DIFFUSION TRANSPORT MODELS

3.1 DIFFUSION THEORY

Matrix diffusion transport models are based on the assumption that solute transport occurs in two types of porosity—mobile and immobile. Conceptually, mobile porosity includes networks of connected fractures and macropores through which water and contaminants are transported by both advective and dispersive processes. The immobile porosity is that in which transport of contaminants occurs through diffusion only; it may include dead-end fractures and pore space, microfractures, and intergranular porosity. The concept of all flow occurring in fractures, and all matrix pores being stagnant imposes some conceptual limitations because not all fractures conduct fluid flow and not all matrix water is stagnant. For this reason, it is best to discuss the matrix diffusion process simply in terms of mobile and immobile porosity—designated by the subscripts m and im, respectively. Figure 3-1 illustrates this concept of matrix diffusion and highlights the fact that rock matrix is not a single homogenous domain, but rather is a complex system that may contain microfractures, mineral grains, porous fracture coatings, and altered zones.

In the classic Fickian approach, movement of contaminants from the mobile porosity domain into the immobile domain can be described by

$$J = -\theta_{\mathrm{im}} D_{\mathrm{eff}} \frac{\partial C_{\mathrm{p}}}{\partial z} \Big|_{z=0}, \tag{3-1}$$

where J is the mass flux rate into the matrix per unit surface area of mobile-immobile interface; θ_{im} is immobile water-filled volumetric water content; D_{eff} is the effective diffusion coefficient; C_{p} is the local concentration in the immobile pore water; and z is distance from the mobile-immobile interface. The value of D_{eff} is a function of solute and solution molecular properties, temperature, and pore geometry. It can be calculated from the formula

$$D_{\mathrm{eff}} = \frac{c}{\tau^2} D_{\mathrm{w}}, \tag{3-2}$$

where, c is the matrix constrictivity factor ($0 \leq c \leq 1$), τ is the matrix tortuosity factor ($\tau \geq 1$), and D_{w} is the free water diffusion coefficient of the solute.

3.2 MATRIX DIFFUSION TRANSPORT MODEL

The general equation describing two-region solute transport with linear reversible sorption, and first-order decay of an aqueous solute in 1D form is

$$\theta_{\mathrm{im}} R_{\mathrm{im}} \frac{\partial C_{\mathrm{im}}}{\partial t} + \theta_{\mathrm{m}} R_{\mathrm{m}} \frac{\partial C_{\mathrm{m}}}{\partial t} = \theta_{\mathrm{m}} D_{\mathrm{m}} \frac{\partial^2 C_{\mathrm{m}}}{\partial x^2} - \theta_{\mathrm{m}} v_{\mathrm{m}} \frac{\partial C_{\mathrm{m}}}{\partial x} - \lambda\left(\theta_{\mathrm{m}} C_{\mathrm{m}} + \theta_{\mathrm{im}} C_{\mathrm{im}}\right), \tag{3-3}$$

where θ_{m} and θ_{im} are the volumetric water contents attributable to the mobile and immobile regions, such that $\theta_{\mathrm{m}} + \theta_{\mathrm{im}} = \theta$, where θ is the total system water-filled porosity. R_{m} and R_{im} are retardation

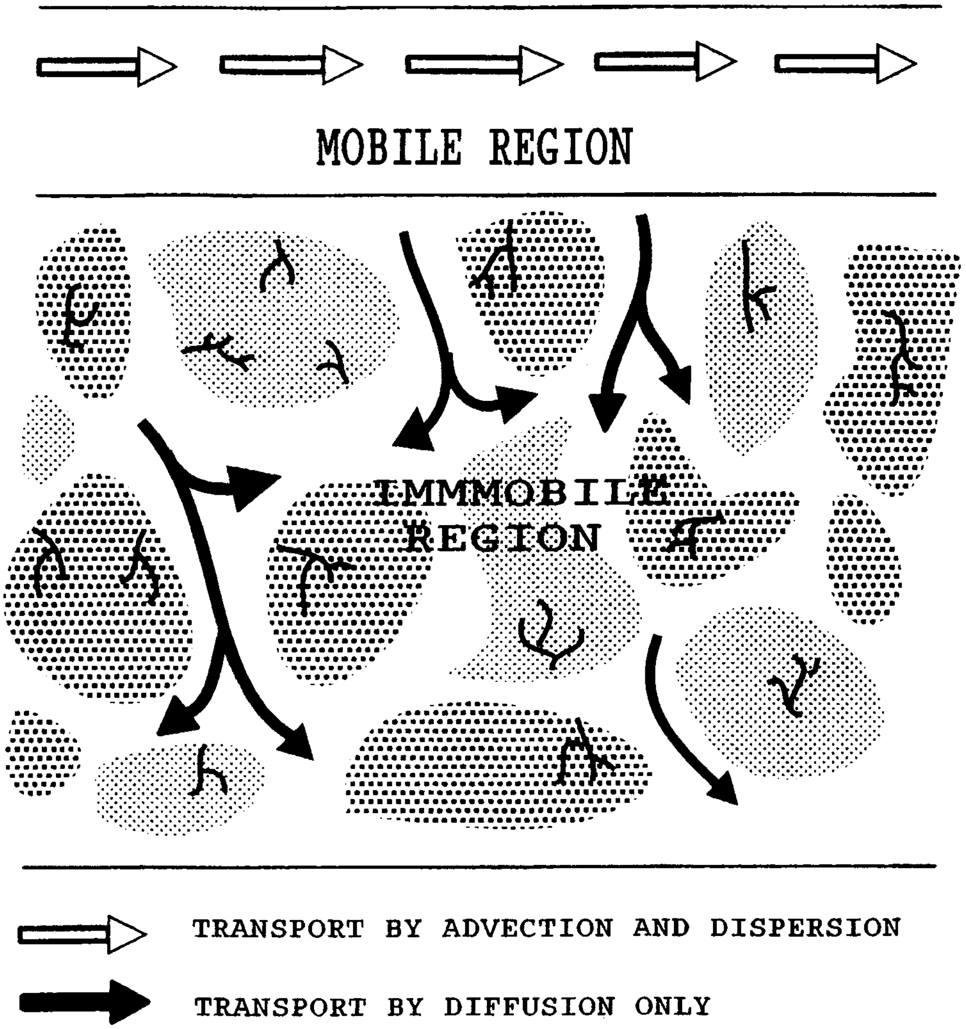

Figure 3-1. Immobile transport regions can consist of an assortment of microfractures, dead-end fractures, and matrix that has varying degrees of cementation and alteration. The result is that diffusive transport is seldom uniform throughout the immobile region. In practice, however, it is often sufficient to use "effective" diffusion coefficients.

factors of the two regions; C_m and C_{im} are the volume-averaged mobile and immobile solute concentrations; D_m and v_m are the macro-scale dispersion coefficient and advection velocity, respectively, for transport through the mobile region; x is distance in the direction of flow; t is time; and λ is a first-order radioactive decay coefficient. Coupling of this mass conservation equation to groundwater flow equations occurs through v_m and the groundwater-velocity-dependent D_m.

The first term on the left-hand side of Eq. (3-3) represents the time rate-of-change of solute mass per unit volume of immobile region. This term may be coupled to either a first-order kinetic rate model, or a diffusion rate model. Here, we discuss only the diffusion rate model. Coupling of Eq. (3-3) to the diffusion rate model requires the introduction of two additional equations. The coupling equations used are dependent upon system geometry, but for fracture-matrix systems, matrix is commonly represented as planar sheets of thickness $2a$, separated by evenly spaced, constant-aperture, parallel fractures of width $2b$, as shown in figure 3-2. For this type of rectangular system geometry, the coupling equations are

$$C_{\mathrm{im}} = \frac{1}{a} \int_0^a C_{\mathrm{a}}(x,z,t)\, dz \tag{3-4}$$

and

$$R_{\mathrm{im}} \frac{\partial C_{\mathrm{a}}}{\partial t} = D_{\mathrm{im}} \frac{\partial^2 C_{\mathrm{a}}}{\partial z^2} - \lambda C_{\mathrm{a}} \tag{3-5}$$

where the immobile diffusion coefficient, D_{im} is equal to the product $\theta_{\mathrm{im}}\ D_{\mathrm{eff}}$, and C_{a} is the local solute concentration in the immobile region.

Table 3-1 lists references for several well-known analytical solutions to variations of this transport model. This list illustrates some of the key differences between the various solutions. These differences include treatment of boundary conditions, dispersion, radionuclide decay, and system geometry.

Analytical solutions are limited in their application to homogenous mobile and immobile regions. In reality, however, fractures are not evenly-spaced and of constant aperture; matrix blocks differ in size and have zones of differing porosity, tortuosity, and sorptive properties. Recent studies (e.g., Hsieh, et al., 1997; Tidwell et al., 1997) have illustrated this point by showing that better model fits to laboratory diffusion experiments are obtained when matrix is divided into multiple domains—each with its respective diffusion coefficient. In practice however, it is often sufficient to assume average or effective matrix properties. Such assumptions are discussed in the following sections.

3.3 TRANSPORT MODEL SENSITIVITY

Breakthrough curves provide a useful means to demonstrate the sensitivity of matrix diffusion transport models to the variables in Eqs. (3-3) through (3-5). Breakthrough curves are plots of predicted concentration versus time for a sorbing or nonsorbing tracer at a given distance from the tracer source. These curves may be generated with using any of the models listed in table 3-1. However, for purposes of this report, it is convenient to use the analytical solution of Rasmuson and Neretnieks (1980) adapted for flow through rectangular voids (van Genuchten, 1985). The complete analytical solution is shown in appendix A. This 1D solution assumes evenly spaced parallel fractures, and a constant concentration source; no decay of the migrating solute is considered. Model variables are lumped into four dimensionless input parameters—P, R, γ, and β—that define the shape of the breakthrough curve. Examination of these dimensionless parameters is useful for understanding the interdependence of the variables in Eqs. (3-3)–(3-5). They are defined as follows:

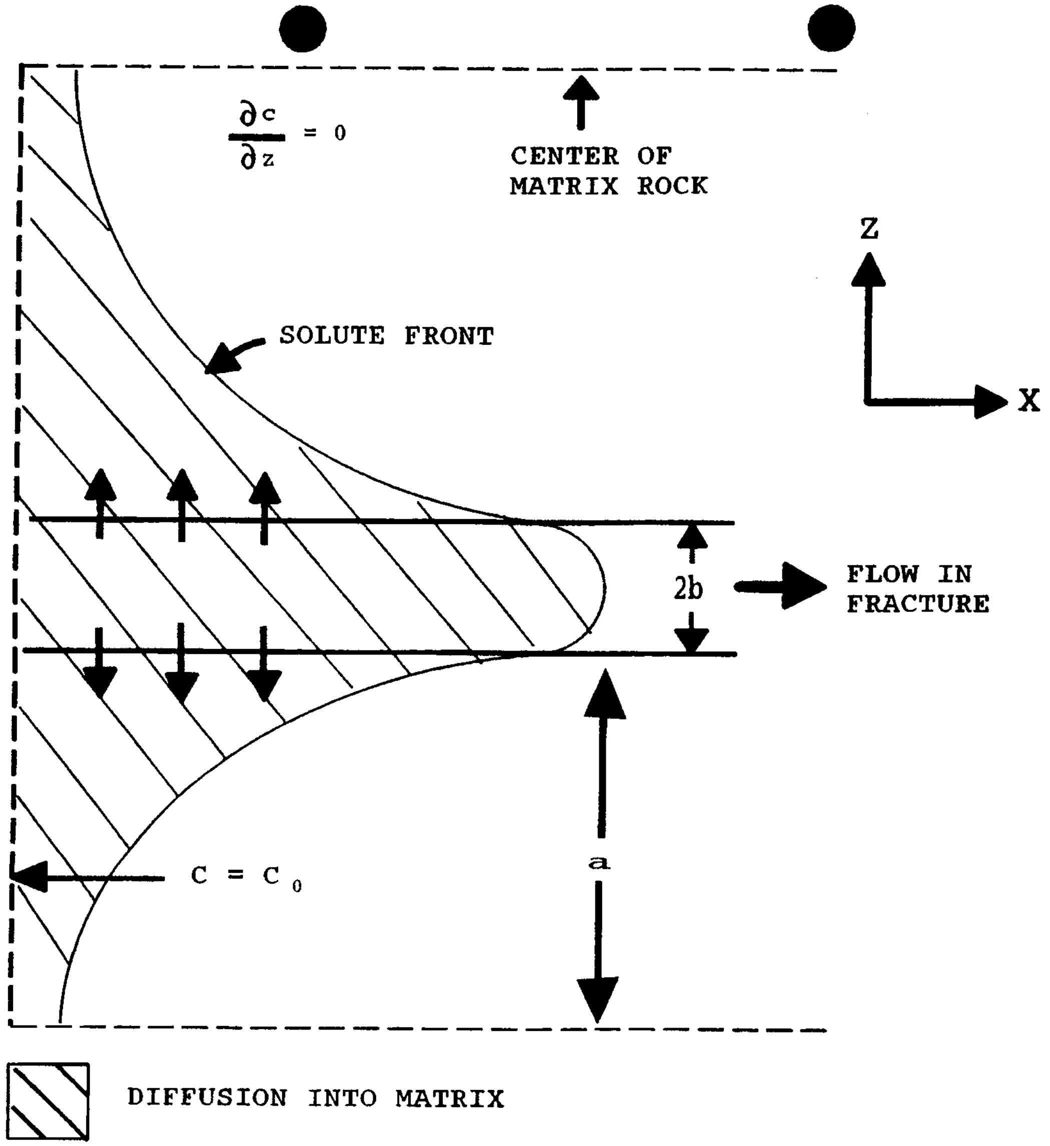

Figure 3-2. Schematic representation of a model for solute transport in a system of parallel fractures.

$$\gamma = \frac{D_{im}\ \theta\ L}{a^2\ q\ R_{im}}, \tag{3-6}$$

$$R = \frac{\theta_{im}\ R_{im} + \theta_m\ R_m}{\theta}, \tag{3-7}$$

$$\beta = \frac{\theta_m\ R_m}{\theta R}, \tag{3-8}$$

and

Table 3-1. Analytical solutions for transport in fractured rock with matrix diffusion

Reference/Model	Flow Geometry and Boundary Conditions	Treatment of Source	Treatment of Radionuclide Decay	Treatment of Mechanical Dispersion
Neretnieks, 1980	1D flow in a single planar fracture with fixed aperture; infinite immobile region. Model solves for aqueous concentration in mobile region.	Allows for exponential decay.	Single decaying species; no decay chains.	No
Tang et al., 1981	1D flow in a single planar fracture with fixed aperture; infinite immobile region. Model solves for aqueous concentration in mobile region.	Allows for exponential decay.	Single decaying species; no decay chains.	Yes
Sudicky and Frind, 1982	1D flow in evenly spaced parallel fractures with fixed aperture; finite matrix domain. Model solves for aqueous concentration in mobile region.	Constant concentration.	Single decaying species; no decay chains.	No (approximate solution); Yes (exact solution)
van Genuchten et al., 1984; (see also: Rasmuson and Neretnieks, 1986)	1D flow in cylindrical macropore of constant radius; approximate solution for infinite cylindrical immobile region; exact solution for finite immobile region.	Allows for exponential decay.	Single decaying species; no decay chains.	No (approximate solution); Yes (exact solution)
Gureghian, 1990/ FRACFLO	2D fracture in x-y plane of fixed aperture; 2D infinite matrix in x-z plane. Model solves for aqueous concentration in both immobile and mobile regions.	Allows for exponential decay. Solutions for single and multiple patch sources, and Gaussian distributed source.	Single decaying species; no decay chains.	No
Gureghian, 1992/ MULTFRAC	1D flow in a single planar fracture; allows for layers, normal to flow, with variable fracture aperture and diffusion properties; infinite immobile region. Model solves for aqueous concentration in both immobile and mobile regions.	Allows for exponential decay, and periodically fluctuating source with exponential decay. Step and band release modes.	Single decaying species; no decay chains	No
Gureghian et al., 1994/ FRAC_SSI	1D flow in a single planar fracture with fixed aperture; infinite immobile region;	Allows for exponential decay. Step and band release modes.	Single parent species; allows user-specified decay chain. Only parent species decays in immobile region.	No

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$$P = \frac{v_{\mathrm{m}} L}{D_{\mathrm{m}}} \approx \frac{L}{\alpha_{\mathrm{L}}} \tag{3-9}$$

where L is distance from the source to the point of observation; α_{L} is longitudinal dispersion length; q is area-averaged fluid flux into the system; R_{m} and R_{im} are mobile region and matrix retardation factors, respectively.

Now that the model parameters have been introduced, the next order of business is to investigate how each parameter affects the prediction of solute transport through fractured rock when varied relative to a base case. The base case represents a "best guess" of conditions at YM, based on properties of the Prow-Pass Bullfrog interval of the C-Hole complex (Geldon, 1996; Flint, 1996), the range of laboratory-determined diffusion coefficients (e.g., Triay et al., 1996), and local hydraulic gradients, (e.g., Luckey et al., 1996). Table 3-2 lists the values for fixed and base case variables used in these analyses. For simplification, R_{m} and R_{im} are assumed to equal 1 as in the case of a nonsorbing solute. For sorbing solutes, R_{im} is likely to be much higher than R_{m} because of the increased surface area available for sorption within the rock matrix.

3.3.1 Limiting Cases

In section 2.2 it was noted that DOE is has proposed the use of an increased effective mobile porosity to account for the effects of matrix diffusion in their PA model without actually having to solve a matrix diffusion model. Presumably, the effective mobile porosity would increase with more rapid matrix diffusion. For this reason, it is useful to examine two limiting cases: (i) flow only in fractures with no matrix diffusion, and (ii) all mobile porosity with no matrix diffusion. Because no matrix diffusion is occurring, a simple equilibrium transport model is used to generate breakthrough curves for these two scenarios. The effective porosity is equal to fracture porosity for the first case ($\theta = 0.0015$), and equal to total porosity for the second case ($\theta = 0.15$).

Figure 3-3 shows the resulting breakthrough curves for these two cases. Note that all breakthrough curves shown in this report represent relative concentration at an observation point 1000 m downstream from a constant-concentration source with an area-averaged fluid flux of 0.15 m/yr. In the first case, when fluid flux occurs only in fractures and there is no matrix diffusion, the average fluid velocity is 100 m/yr resulting in a breakthrough time of 10 yr, with the earliest contaminants arriving in less than 5 yr. In the second case, when the total porosity (i.e., fracture and matrix) is available for fluid flow, average fluid velocity is only 1 m/yr resulting in a breakthrough time of 1,000 yr and arrival of the earliest contaminants at around 500 yr.

It is interesting to note that a breakthrough curve for the matrix diffusion model will approach the curve for the first case when matrix diffusion is very slow ($\gamma \rightarrow 0$) and it will approach the curve for the second case when matrix diffusion is very fast ($\gamma \rightarrow \infty$). This is likely the rationale behind DOE's suggested use of an increased effective porosity to simulate the effects of matrix diffusion. However, for the conditions used to generate the breakthrough curves in figure 3-3, the entire spectrum of breakthrough curves that can be generated by changing the effective porosity must fall within the area bounded by the two limiting cases shown. Conversely, the shapes of the breakthrough curves for the matrix diffusion model are not so constrained, as will be shown in the following section. This fact should be taken into consideration when evaluating the appropriateness of DOE's increased-effective-porosity approach.

Table 3-2. Parameters used for matrix diffusion model sensitivity analysis

Area-averaged Flux (q)	0.15 m/yr	fixed for all scenarios
Total Porosity (θ)	0.15	fixed for all scenarios
Length Scale (L)	1,000 m	fixed for all scenarios
Retardation Factor ($R_m = R_{im}$)	1.0	base case value
Dispersion Length (α_L)	50 m	base case value
Matrix Block Half-Width (a)	0.5 m	base case value
Fracture Porosity (θ_m)	0.0015	base case value
Immobile Diffusion Coefficient (D_{im})	10^{-11} m^2/s	base case value
Resulting Base case Model Parameters	—	—
γ	1.3	base case value
β	0.01	base case value
P	20	base case value

3.3.2 Sensitivity to γ

The parameter γ is central to this discussion because it is the only parameter that contains the immobile diffusion coefficient, D_{im}. It is useful to think of γ as a measure of the importance of matrix diffusion compared to the advective flux of solutes through the system. A higher γ-value implies more rapid diffusion into the matrix; when γ approaches zero, then very little matrix diffusion occurs and solutes remain in the mobile region where they can travel through convection and diffusion. Notice in Eq. (3-6) that, in addition to the diffusion coefficient, the value of γ is also proportional to the length-scale of the problem and the total porosity; it is inversely proportional to the liquid flux rate, the immobile region retardation factor, and the square of a.

Figure 3-4 includes the breakthrough curves for the two limiting effective porosity cases where no matrix diffusion occurs. Three additional curves show how changes in γ affect the arrival time of a nonsorbing tracer. The base case curve is the result of input parameters listed in table 3-2. Two additional curves are for slow and rapid diffusion cases: they have γ values based on a D_{im} that is one-tenth, and ten-times as great as that of the base case, respectively. Notice that slow diffusion moves the shape of the breakthrough curve from the base case toward the shape of the fracture-flow-only curve; fast diffusion causes the breakthrough curve to move toward the shape of the all-mobile-porosity curve.

Effective matrix block width determines the value of a. Because γ is inversely proportional to the square of a, the matrix diffusion model is more sensitive to matrix block size (i.e., spacing between flowing fractures) than it is to the value of D_{im}. At YM, distances between flowing fractures are not

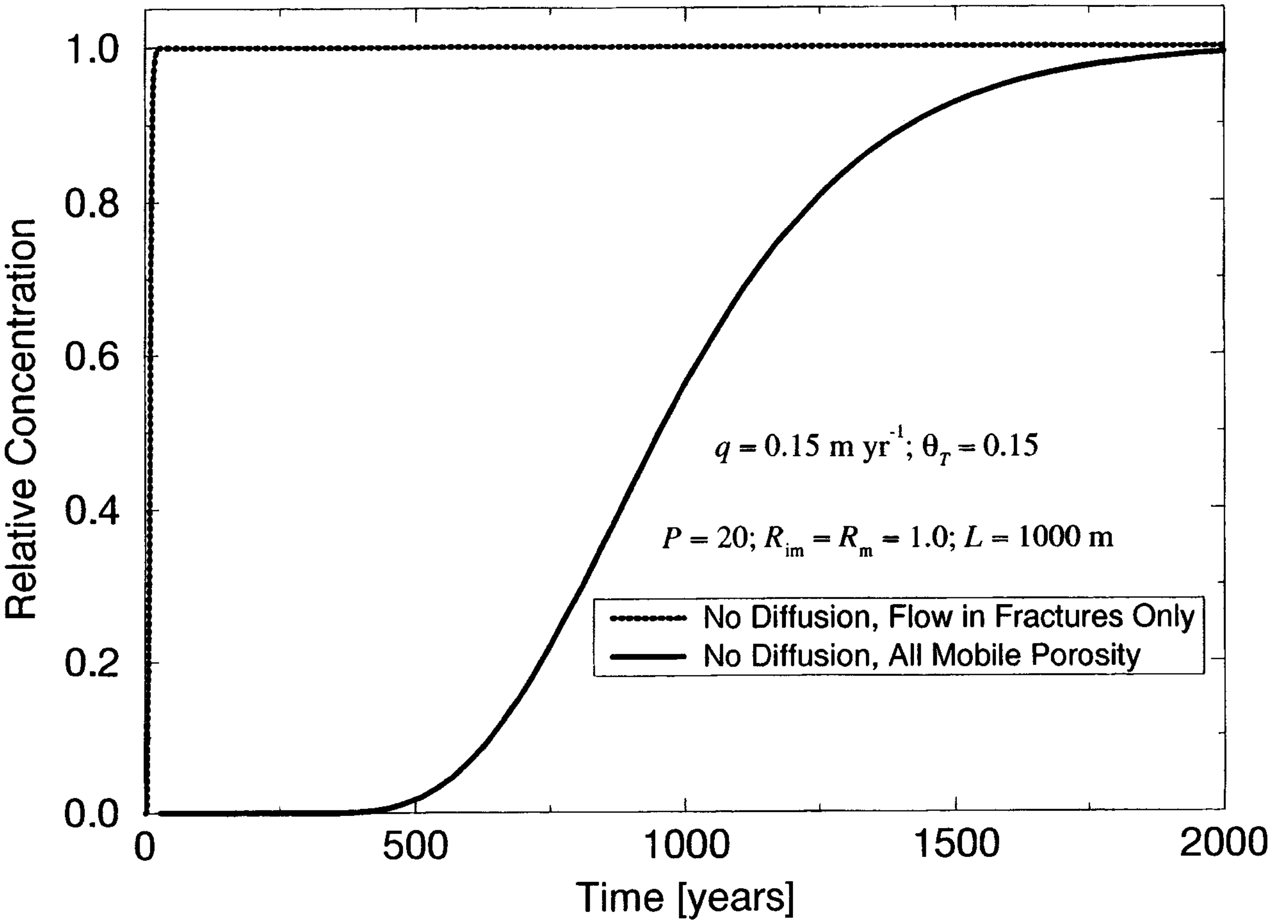

Figure 3-3. Breakthrough curves show arrival times for a nonsorbing tracer for two extreme cases where matrix diffusion does not occur; in the first case (dotted) effective porosity is equal to fracture porosity; in the second case (solid) all porosity is considered mobile.

well-characterized. This causes considerable uncertainty in estimating a range of possible values for *a* at YM, and is arguably the greatest source of uncertainty in estimating values for γ.

Because the value of γ is inversely proportional to R_{im}, increases in R_{im} result in smaller γ-values. Upon examining the model sensitivity to γ in figure 3-4, one might conclude that an increase in R_{im} could actually result in *earlier* solute arrival times. However, this counterintuitive behavior is only possible if R_{im} could increase without an accompanying increase in the overall retardation factor, *R* (i.e., an increase in θ_{im} R_{im} with an offsetting decrease in θ_m R_m). Generally, this would not be the case. Sensitivity of the matrix diffusion model to *R* is discussed in the following section.

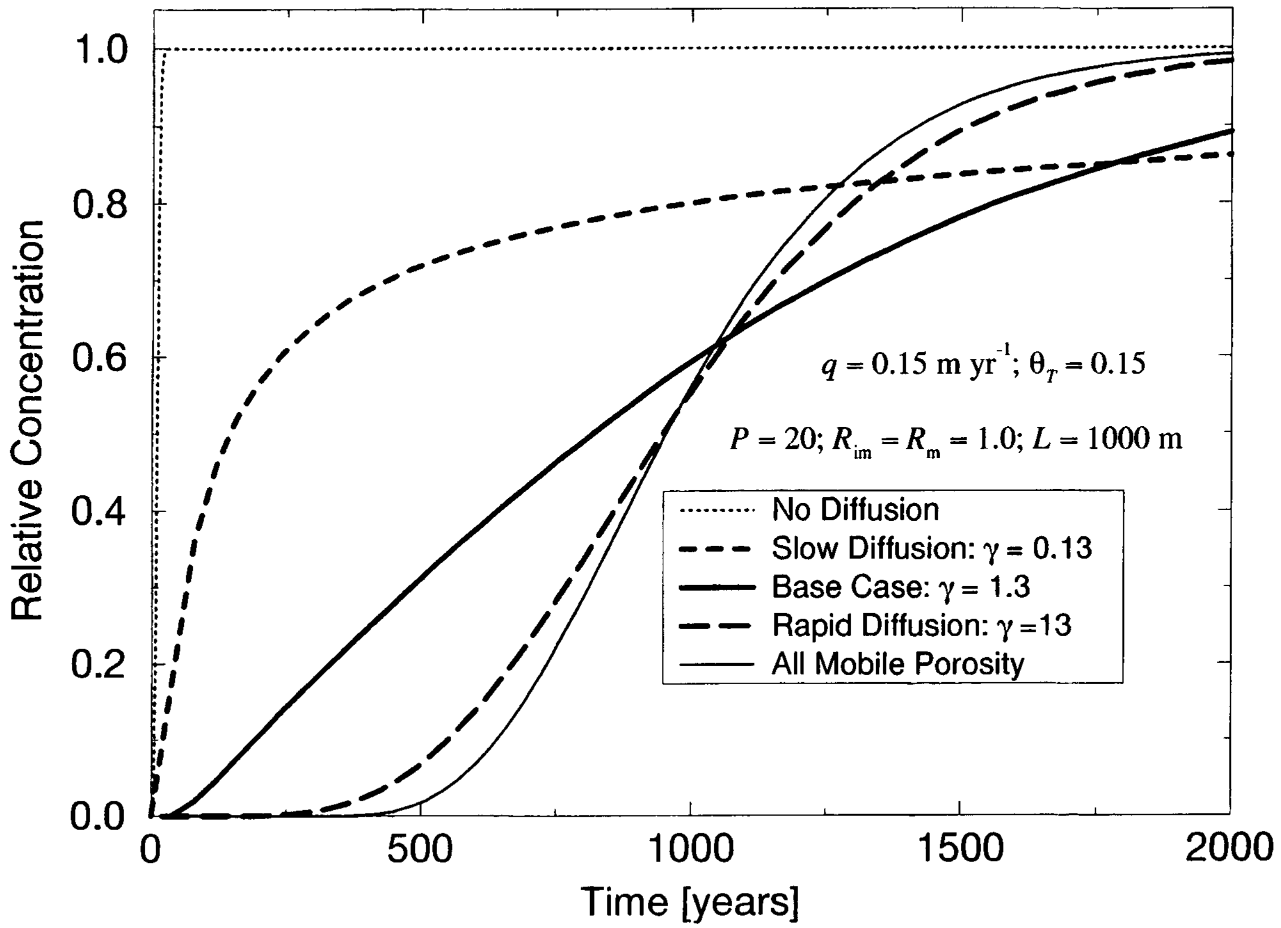

Figure 3-4. Breakthrough curves show arrival times for a nonsorbing tracer under various assumed matrix diffusion scenarios. As matrix diffusion occurs more rapidly, the shape of the breakthrough curve approaches that of the case with all mobile porosity.

3.3.3 Sensitivity to *R*

Figure 3-5 demonstrates the effect of an increased overall retardation factor on the base case scenario. For these analyses, it is assumed that R_{im} remains equal to R_m. Therefore, an increase in the value of R is accompanied by a proportional decrease in the value of γ. Notice that the earliest solute arrival time is not significantly affected, however the solute concentrations are attenuated considerably. This effect of increased R on the matrix diffusion transport model is quite different from the effect on an equilibrium model, where breakthrough curves retain their exact shape but arrival times are delayed.

Depending on host rock mineralogy and water chemistry, retardation factors for many sorbing radionuclides (e.g., Cs, Pu, Am, Sr, Ba) can be much higher than the $R = 10$ shown in figure 3-5 (e.g., Triay et al., 1996). Hence, matrix diffusion could result in considerable attenuation of sorbing radionuclides over periods on tens of thousands of years, given the scale and flow characteristics of the base case.

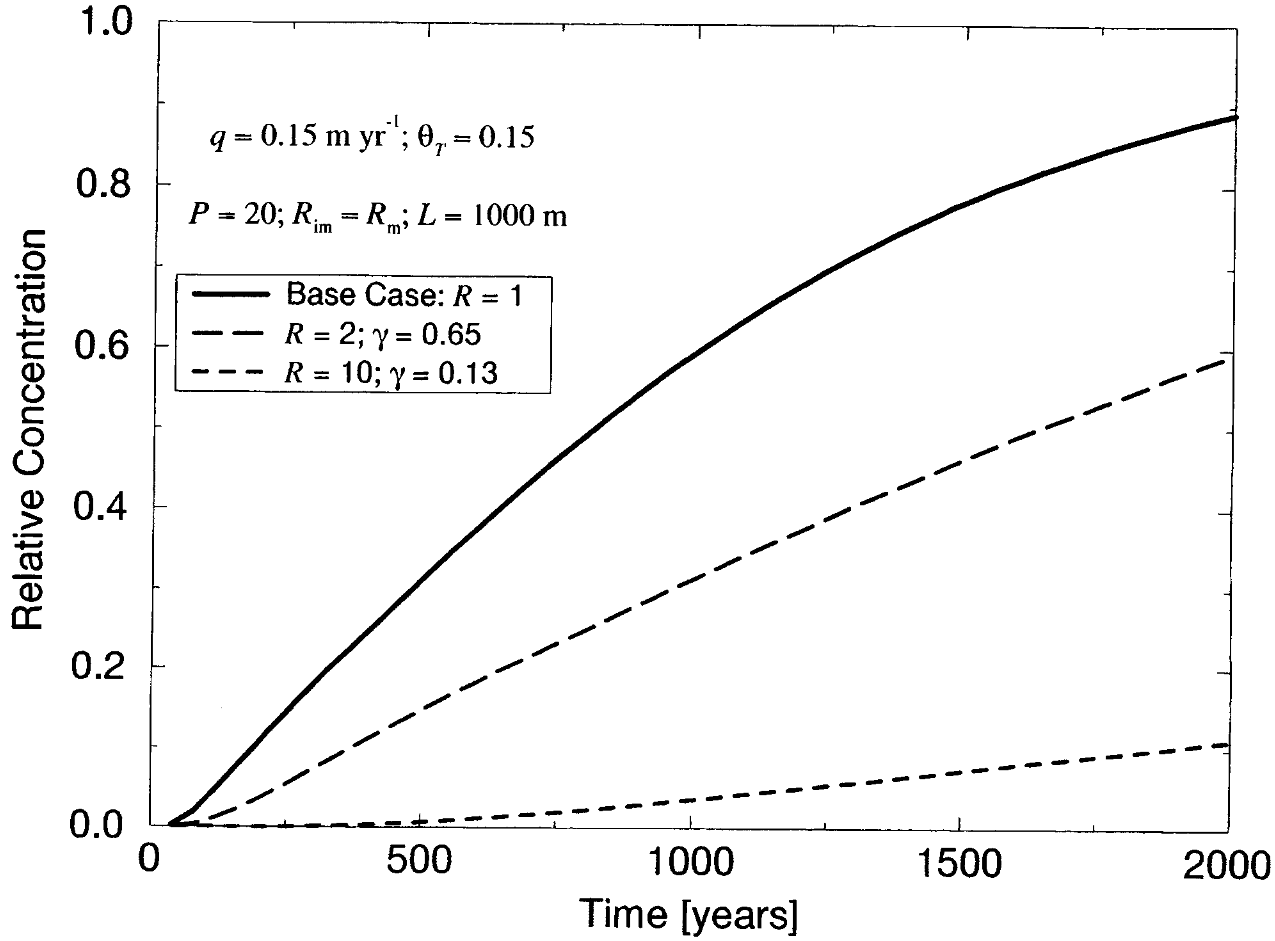

Figure 3-5. Increases in the retardation factor from the base case result in significant attenuation of solute the concentration. In the plots shown here, it is assumed that an increase in R implies a proportional increase in R_{im}. Thus, the value of γ decreases with increasing R.

3.3.4 Sensitivity to β

The β parameter can be thought of as the fraction of the total storage capacity due to the fracture. If the retardation coefficients in the fracture and matrix are equal, then β is simply the fraction of mobile porosity. If β is equal to one, then all porosity is mobile and matrix diffusion becomes irrelevant. Figure 3-6 illustrates the effect of increasing β relative to the base case scenario. With the γ parameter held constant, an increase in β could represent either a greater fraction of mobile porosity (e.g., increased fracture aperture), or more sorption in the mobile region.

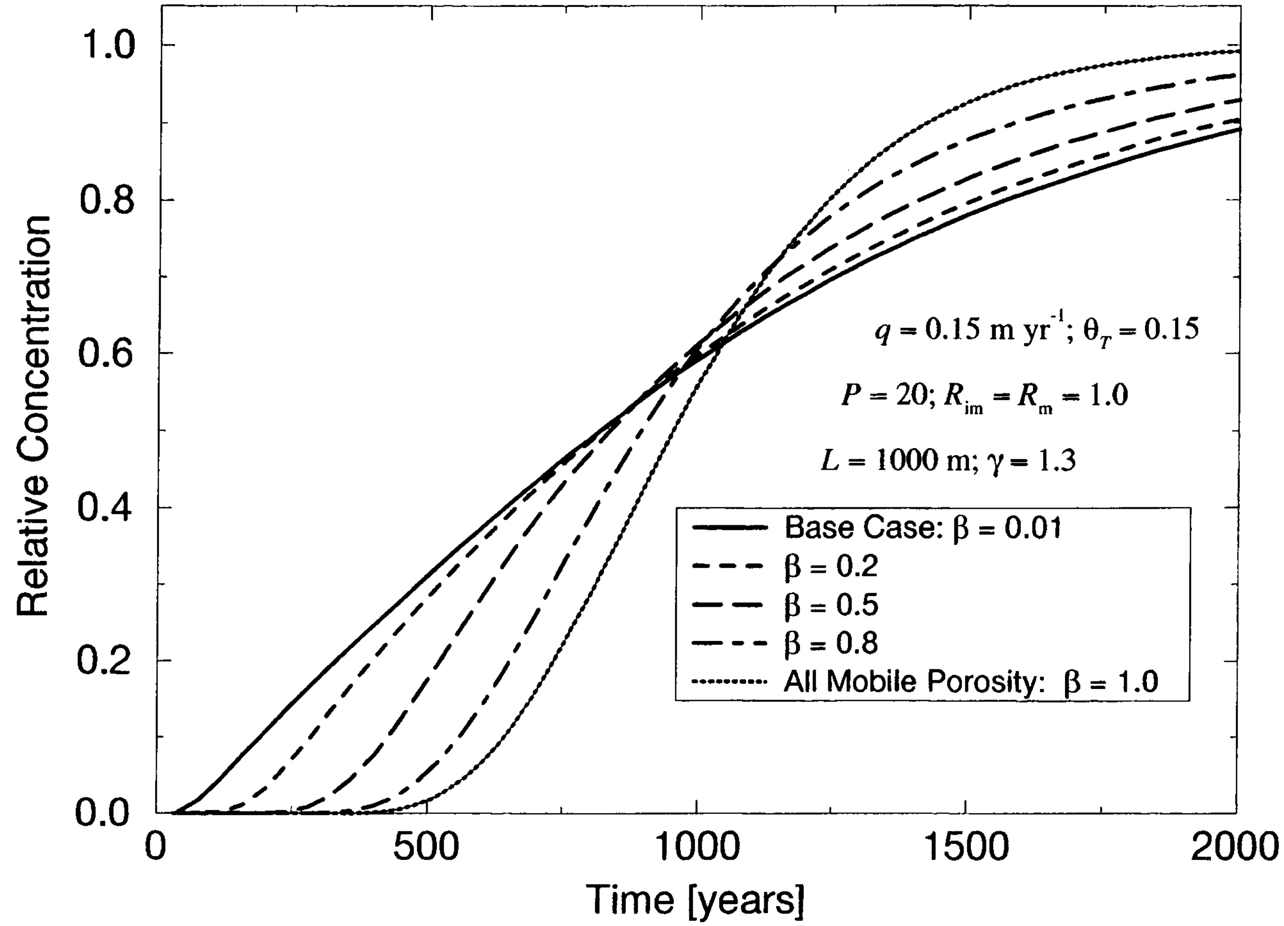

Figure 3-6. Breakthrough curves show the effects of different fractions of mobile porosity (β). For the γ-value used in this analysis, decreases in the value of β below about 0.1 had no significant effect on curve shape or arrival time.

As the value of β is increased, the effects of matrix diffusion become less distinguishable from the case where all porosity is mobile. For the conditions assumed for this analysis, a value of β as low as 0.0001 was not discernibly different from the base case. This latter observation is important because, with the assumed low fracture porosities at YM, the value of β is likely to be low—especially if the immobile region retardation factor is high relative to that of the mobile region. Because the model is less sensitive to β when β is low, it may be sufficient for PA purposes to simply estimate a lower bounding value.

3.3.5 Sensitivity to *P*

Many of the model solutions listed in table 3-1 are based on a simplifying assumption that the effects of mechanical dispersion in the mobile region are negligible compared to the effects of matrix diffusion. This assumption can be tested by examining model sensitivity to the parameter P. Defined by Eq. (3-9), P is the Peclet number for the mobile region; it represents the ratio of the average advection velocity to the time scale for mechanical dispersion. Higher values of *P* infer less mechanical dispersion in the mobile region.

Figure 3-7 shows the effect of the value of *P* on the shape of the breakthrough curve. For the cased considered, *P*-values of 2.0 and 2,000 correspond to dispersion lengths of 500 m and 0.5 m, respectively, whereas the base case *P* value corresponds to a dispersion length of 50 m. This range of dispersion lengths conservatively brackets the range of observed dispersion lengths for the length scale under consideration (Gelhar et al., 1992). When there is very little mechanical dispersion ($P = 2{,}000$), results are not significantly different from the base case. However, when there is a great deal of mechanical dispersion ($P = 2.0$), tracer arrival occurs somewhat earlier.

3.4 FIRST-ORDER APPROXIMATION OF MATRIX DIFFUSION

The PA model currently used by the NRC incorporates NEFTRAN II (Olague et al., 1991), which uses a first-order kinetic model as an approximation of the matrix diffusion model. In first-order kinetic transport models, Eqs. (3-4) and (3-5) are replaced by a single equation:

$$R_{\mathrm{im}}\theta_{\mathrm{im}}\frac{\partial C_{\mathrm{im}}}{\partial t} = \alpha\left(C_{\mathrm{m}} - C_{\mathrm{im}}\right) , \tag{3-10}$$

where α is an empirical rate coefficient that depends in some way on matrix block size and the immobile diffusion coefficient. A key assumption of first-order models is that solute concentration is uniform throughout the entire matrix block. This implies a uniform solute concentration within each matrix block. In other words, once a solute molecule is transported across the mobile-immobile interface, it is instantaneously well mixed within the immobile pore water. Of course, this is not true; however, depending on diffusion rates and matrix block size, it is often a reasonable approximation. A method for estimating α from matrix block and diffusion properties was developed by van Genuchten (1985) and has the form

$$\alpha = \frac{\theta_{\mathrm{im}} D_{\mathrm{im}}}{\mathrm{f}\ a^2} , \tag{3-11}$$

where f is a geometry-dependent shape factor. For flow through parallel fractures, as in the base case, f is equal to 0.28.

When the first-order approximation is used, the model parameter γ [Eq. (3-6)] is replaced by another dimensionless parameter, ω, where

$$\omega = \frac{\alpha L}{q} = \frac{\theta_{\mathrm{im}} D_{\mathrm{im}} L}{\mathrm{f} q a^2} . \tag{3-12}$$

Figure 3-8 compares breakthrough curves for two matrix diffusion scenarios with their associated first-order approximations calculated from the matrix diffusion parameters using Eq. (3-12). When the value of γ is increased (e.g., fast diffusion, low immobile sorption, or small matrix blocks), the

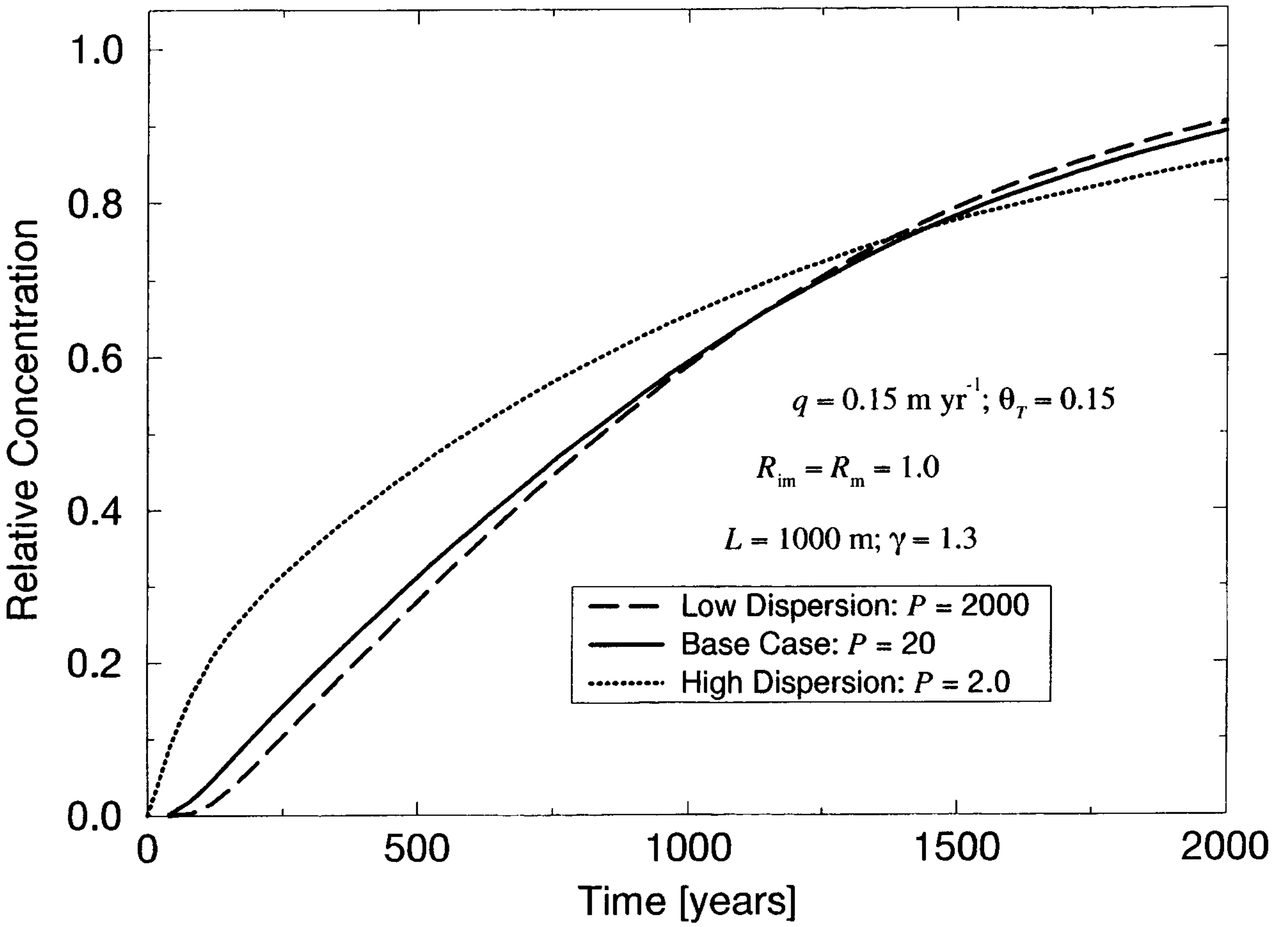

Figure 3-7. Breakthrough curves show the effect of mechanical dispersion on the arrival time of a nonsorbing tracer. The case with low dispersion has a slightly later arrival time than the base case. The high-dispersion case has an earlier arrival time and a faster increase in concentration than the

agreement between the two models improves, and is quite good for the base case scenario. For small values of γ, the first-order approximation tends to overestimate solute concentrations at early times, and overestimate them at late times; however, the early overestimation is likely to be a conservative error, and the late underestimation is within about 10-percent of the matrix diffusion model.

3.5 APPLICABILITY OF MATRIX DIFFUSION MODEL ASSUMPTIONS

The use of a matrix diffusion model to describe transport through saturated and unsaturated geologic media is only as valid as the assumptions upon which it is based. These assumptions include

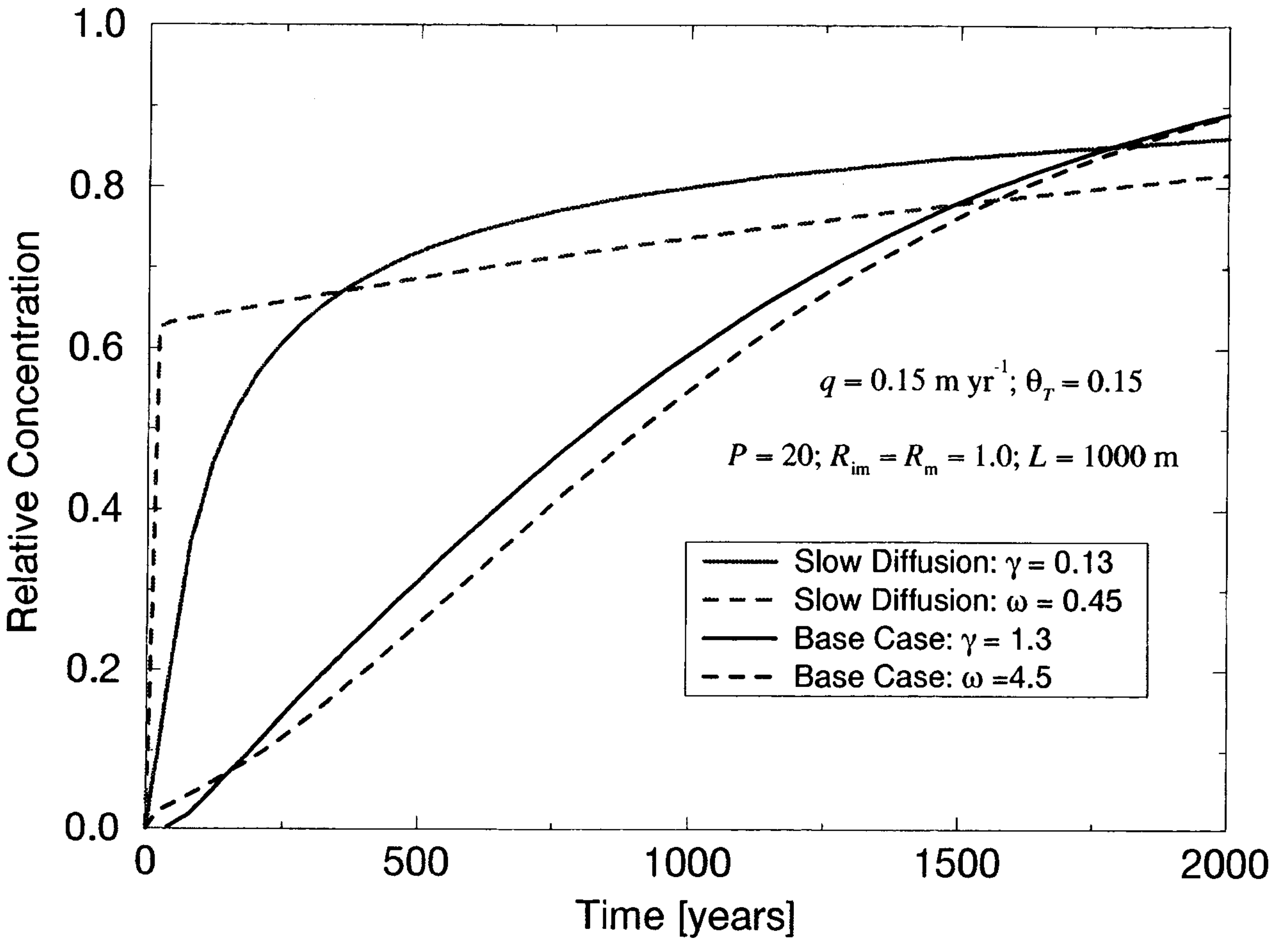

Figure 3-8. Breakthrough curves show a comparison of matrix diffusion models (solid lines) and their first-order approximations (dashed lines).

(i) the existence of mobile and immobile transport domains; (ii) uniform flow through uniform fractures, and (iii) uniform diffusion in the immobile region. Additional assumptions are introduced in the various analytical solutions to the matrix diffusion model—for example, the assumption that dispersion in the mobile region is negligible. Another common assumption used in analytical solutions is that flow occurs in either a single fracture (infinite immobile region) or in evenly spaced parallel fractures (finite immobile region). The applicability of these assumptions is discussed in the following subsections.

3.5.1 Existence of an Immobile Region

The coupling of Eqs. (3-3) and (3-5) is based on the existence of mobile and immobile transport domains. This implies an assumption that advective mass transport into the rock matrix is negligible compared to diffusive mass transport. However, even the most densely welded rocks found at YM have greater-than-zero matrix permeability. As such, under a hydraulic gradient, the advection through matrix pore water must also be greater than zero. The assumption of negligible matrix advection can be tested by examining the ratio (B) of the time scale for advective transport within rock matrix to the time scale for diffusive transport. Assuming a cube-shaped matrix block of width 2a, and diffusion into the matrix from a planar fracture occurs normal to the direction of advection, this ratio can be express as

$$B = \frac{v_r a}{D_{\mathrm{im}}} \tag{3-13}$$

where v is advection velocity within the rock matrix, and a is the matrix block half-width in the direction of diffusion. If B is much less than one, then diffusion is the dominant transport mechanism.

For rocks in the saturated zone beneath YM, a range for v can be estimated from a hydraulic gradient range of 0.0001 to 0.0003 (TRW Environmental Safety Systems, Inc., 1997), and a matrix hydraulic conductivity range of about 10^{-11} to 10^{-9} m s^{-1} (Flint, 1996). Laboratory-measured values of D_{im} for rocks at YM range from about 10^{-11} to 10^{-10} m^2 s^{-1} (Triay et al., 1996). Typical values for a range from about 0.2 to 0.8 m, based on a fracture spacing survey in the Exploratory Studies Facility (ESF) at YM (Anna, 1997). These numbers yield a range of values for B from 2×10^{-6} to 0.024. This range suggests that the assumption of negligible advection in the matrix is valid in areas of highly-fractured low-permeability rock layers at YM. It should be noted that some thin layers of high matrix permeability exist in the saturated zone beneath the proposed repository (e.g., Calico Hills vitric, Bedded Tuff). Flow in these layers is not dominated by fractures, so matrix diffusion is not an issue.

3.5.2 Uniform Flow through Uniform Fractures

Fractures are seldom of uniform aperture and many fractures are “dead-end” fractures that are not interconnected to a continuous fracture network. The result of variability in fracture properties is the formation of multiple preferential flow paths and considerable variation in advection velocities. This has three implications for the use of a matrix diffusion model: (i) multiple preferential transport pathways challenge the assumption of a uniform mobile continuum, (ii) mobile porosity cannot be estimated from total fracture porosity, and (iii) not all matrix block surface area is available for advected solutes to diffuse into.

Fortunately, in the case of item (i), if the scale of a transport model is larger than the scale of heterogeneity in fracture flow velocity and path length, then the effect of the multiple preferential flow paths can be treated as simple mechanical dispersion. There are two reasons for this: first, characteristics of the multiple flow paths tend to be averaged out; second, more flow paths are taken into consideration and their individual effects tend to be smoothed out. Thus, as long as the scale of the transport problem under consideration is sufficiently large, it should be reasonable to treat heterogenous flow patterns as part of the mechanical dispersion process.

Mobile porosity cannot be estimated from fracture porosity because, quite simply, many fractures do not transmit significant quantities of water. Additionally, as previously mentioned, not all matrix porosity is stagnant. For these reasons, the concepts of mobile and immobile porosity are preferable to fracture and matrix porosity in this context. Estimates of effective mobile porosity can be obtained by fitting a flow and transport model (e.g., Moench, 1995) to early breakthrough curve data from nonsorbing tracer tests. For example, Geldon et al. (1997) used conservative tracer data to estimate a mobile porosity of 0.086 for the Bullfrog-Tram interval of the C-Hole Complex at YM. This mobile porosity estimate is much higher than fracture porosity. Given the ranges of fracture frequency and aperture measured in the near YM (Anna, 1997), fracture porosities should range from about 10^{-6} to 10^{-2}. It is not clear why the mobile porosity estimated from this tracer test is so much higher than the estimated range of fracture porosity. One reason may be that the Tram interval of the C-Holes is intersected by a zone of fault breccia which would have a higher-than-usual mobile porosity. Additionally, one cannot discount the possibility that mobile porosity estimates from tracer tests are biased by the assumption of an ideal flow velocity field.

Even if effective mobile porosity can be determined with confidence, the effect of preferential flow pathways on the system geometry must be taken into consideration. When contaminants are transported in isolated channels, not all of the fracture-matrix interface is contacted by the contaminant. Rasmuson and Neretnieks (1986) proposed that such preferential flow paths were analogous to flow in cylindrical channels and they developed an analytical solution for flow in such a system. This solution is listed in table 3-1.

The previous discussion highlights the important role that fracture properties play in development of dual-porosity models to describe solute transport through fractured rock. Unfortunately, it is rarely possible to fully characterize fracture network properties that might result in preferential flow pathways.

3.5.3 Uniform Diffusion in the Immobile Region

Most analytical solutions to dual-porosity transport models assume uniform diffusion properties throughout the immobile region. In reality, the immobile region may contain such heterogenous features as dead-end macro-pores, surface coatings and altered surfaces, microfractures within the matrix, and different degrees of matrix cementation. The result is that contaminants diffuse at different rates in different areas of the immobile region. Tidwell and others (1997) and used x-ray tomography techniques on core samples of Culebra Dolomite to verify that a brine tracer did indeed diffuse through the samples at different rates. Hsieh et al. (1997) were able to obtain better model fits to breakthrough curves when multiple diffusion coefficients were used instead of a single diffusion coefficient.

The importance of considering multiple diffusion rates for larger-scale transport is not clear. On the scale of inter-well tracer tests, it is often difficult to show that matrix diffusion is occurring at all. Trying to elucidate multiple diffusion rates from these tracer tests may not be a productive endeavor because of the potential for nonunique solutions. Future modeling studies could be useful for determining whether there is a need to consider multiple diffusion rates.

3.5.4 No Mechanical Dispersion

Model solutions that neglect macro dispersion in the mobile region (e.g., Neretnieks, 1980; Gureghian, 1990, 1994; Gureghian et al., 1992)—zero-dispersion models—can be expected to give results similar to the $P = 2{,}000$ scenario (figure 3-6), which is not significantly different from the base case. Thus, if mechanical dispersion at YM can be bounded as being "average" or low (e.g., $P \geq 10$), as the base case scenario is assumed to be, neglecting dispersion should not significantly bias transport predictions. Peclet numbers estimated from nonsorbing tracer tests at the C-Hole complex are estimated to be in the range of 11 to 15 (Geldon et al., 1997). On very large scales, Peclet numbers are likely to

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be somewhat higher, because the dispersion length eventually reaches an asymptotic value as the length scale continues to increase. Therefore, zero-dispersion matrix diffusion models may be sufficient for transport predictions in the saturated zone at YM. In the unsaturated zone, however, the nature and magnitude of mechanical dispersion is highly uncertain due to the intermittent nature of infiltration.

3.5.5 Finite versus Infinite Immobile Region

Many analytical solutions to the matrix diffusion model are based on an assumed infinite immobile region (e.g., Neretnieks, 1980; Tang et al., 1981). An infinite immobile region is analogous to flow in a single fracture that bisects an infinite matrix block; hence, diffusing solutes are unhindered by boundary effects. These solutions have the advantage of being less computationally intensive because they require less numerical integration; however, the assumption of an infinite immobile region is only reasonable when values of γ are less than about 0.1 (Gureghian, 1990). Therefore the assumption of an infinite immobile region would be unreasonable for the base case, which has a γ-value of 1.3. However, for solutes that are strongly sorbed, the value of γ would be much smaller than it is for the nonsorbing base case scenario.

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4 LABORATORY AND FIELD STUDIES

4.1 LABORATORY STUDIES

In order to effectively model solute transport through fractured rock, it is important to have reasonable estimates of diffusion coefficients for each radionuclide of concern and for each rock type modeled. In this section, laboratory methods and results of several YM studies are reviewed. Plans for future laboratory work and applicability to field conditions are also discussed.

4.1.1 Existing Data

Some of the earliest measurements of solute diffusion in rocks from YM were conducted by Walter (1982, 1985) who used a diffusion cell method. A diffusion cell is basically two chambers, separated by a rock sample. A known concentration of a solute is added to one chamber, and solute-free water is added to the opposite chamber; the rate of solute migration from one chamber to the other is then fit to a diffusion model. Based on these experiments, Walter concluded that Eq. (3-2) holds true for tuffaceous rocks from YM. That is, effective diffusion coefficients were proportional to free-water diffusion coefficients. He calculated a range of values for D_{eff} from 2×10^{-11} to 1.7×10^{-10} m^2/s for nonsorbing sodium halides and sodium pentaflourobenzoate (PFBA). Total porosity was found to be the principal factor accounting for variation in D_{eff}. The lumped parameter c/τ^2, which ranged from 0.1 to 0.3, had a fair correlation with median pore diameter, as measured by mercury intrusion.

Additional investigations conducted by Walter include: osmosis experiments, assessment of multicomponent effects on diffusion, and a bench-scale fracture flow experiment. Osmosis experiments with YM tuff revealed pressure drops across samples that increased with increasing concentration gradient. Osmotic pressure results when water molecules can travel more freely through a porous media than ionic species that are dissolved in it. Ionic species are restricted when negatively charged mineral surfaces repell anions, thus effectively reducing the pore diameter from the perspective of an anion. This anion-exclusion process could significantly inhibit the diffusion of large anions.

The computed correlation matrix for various tracers revealed that, although there is coupling of diffusion fluxes between all ionic species, multi-component diffusion is a second-order effect that did not significantly affect experiment results.

Results of a bench-scale fracture flow experiment led Walter (1985) to conclude that the transport of ionic tracers was affected by diffusion into the tuff matrix, whereas the transport of a particulate tracer did not appear to be affected by diffusion.

More recently, Triay et al. (1996) performed laboratory diffusion experiments on tuff samples from YM for a variety of radionuclides. Two types of diffusion experiments were conducted: diffusion cell experiments and rock beaker experiments. Rock beaker experiments are similar to diffusion cell experiments, except the solute chamber is formed by the rock itself which is machined into a cup shape. Rock beakers were pre-saturated with solute-free water, tracer was added to the cup, and the observed dilution of solute in the cup was fit to a diffusion model. Because of the radial geometry of the rock beakers, Triay and others used a numerical model to solve for the diffusion coefficient. An analytical solution was used for the diffusion cell experiments. Batch sorption experiments were also conducted to determine distribution coefficients for the sorbing radionuclides.

Nonsorbing radionuclides used in the rock beaker experiments were tritiated water (HTO), and pertechnetate (TcO_4^-), a large anion. The sorbing species used in the experiments were Np, Am, Sr, Cs, and Ba. Estimated values of D_{eff} ranged from 1×10^{-10} to 3.5×10^{-10} m^2/s for HTO, and from 1×10^{-11} to 4.9×10^{-11} for TcO_4^-. The order of magnitude difference between these nonsorbing tracers was attributed to the effects of anion exclusion and the fact that TcO_4^- is a much larger molecule than HTO.

Diffusion coefficients were not estimated for the sorbing species. Instead, observed dilution curves were compared to dilution curves calculated based on the average D_{eff} for HTO of 2×10^{-10}, and measured distribution coefficients. It was found that observed dilution of the sorbing species in the rock beakers was always faster than the calculated dilution, and therefore, use of the HTO diffusion coefficient for sorbing radionuclides was thought to be a conservative assumption (i.e., the assumption will predict slower matrix diffusion).

Diffusion cell experiments of Triay et al., (1996) used nonsorbing HTO and TcO_4^-, and variably sorbing, U(VI), Np(V), and Pu(V). Following are several of their key findings:

- Diffusion occurred at slower rates in devitrified tuff than in zeolitized tuff.
- The large anion TcO_4^- always diffused slower than HTO
- Pu migration was so dominated by sorption that it never reached the opposite side of the diffusion cell.
- Np(V) and U(VI) diffusion was affected by tuff type and water chemistry (i.e., variable sorption).
- In cases where Np(V) did not sorb, it diffused at a rate comparable to that of TcO_4^-

An important conclusion of Triay et al. (1996) was that observed diffusion of sorbing radionuclides was consistent with a conceptual model in which diffusion occurs in two stages. For example, solutes diffuse first through larger intercrystalline pores or microfractures before they diffuse into the narrower intracrystalline pores. It is not clear whether this proposed two stage diffusion process can be approximated with a single effective diffusion coefficient. It is also unclear why the nonsorbing solutes did not exhibit this two-stage-diffusion behavior. One possible explanation could be that the first stage of diffusion in the rock beaker experiments occurred along discrete pathways (e.g., fingering). This would cause relatively small surface sorption in the matrix, but the surface area of the interior cup wall would be large. The result would be an initially rapid dilution of sorbing solutes that would not be seen in nonsorbing solutes. This may also explain why dilution of sorbing radionuclides occurred faster than was predicted using the D_{eff} for HTO.

Multiple-rate diffusion was observed directly in experiments conducted by Tidwell et al. (1997), who used x-ray tomography to visualize diffusion of a brine solution through low-permeability, low-porosity dolomite. They observed that variability of solute migration into a rock sample was associated with variability in porosity and the presence of microfractures. For samples that exhibited multiple-rate diffusion, the diffusion coefficients used to fit observed solute migration data varied by about a factor of two, depending on whether a better fit was desired for early time or late time data. From a visual examination of the model fits obtained by Tidwell et al., it appears that a single diffusion coefficient could give a reasonable fit to the overall migration data. It should be noted that the experiments of Tidwell et al. have yet to undergo peer review and their data were not collected under a qualified quality assurance program.

4.1.2 Future Laboratory Studies

According to Triay et al. (1996), the YM Study Plan calls for diffusion experiments on unsaturated tuffs. The Plan proposes a method in which tracers are allowed to diffuse into unsaturated samples for a given time. The samples would then be frozen and cut into sections; the sections would be analyzed for tracer concentration, and these data would be fit to a diffusion model to elucidate diffusion rates. These planned experiments are critically reviewed by Triay et al. who point out the great lengths of time it would take to obtain significant diffusive transport into an unsaturated rock matrix. They propose a much simpler indirect method of measuring electrical conductivity in a potentiostatic or galvanostatic mode, coupled with the Nernst-Einstein relationship, which provides reliable diffusion coefficients in electrolyte solutions.

Electrical conductivity and resistivity methods are well established for use in saturated samples (e.g., Miller 1972). In fact, resistivity measurements were used by Walter (1982) for saturated samples from the vicinity of YM. Electrical conductivity is related to diffusive migration of ions because, like diffusivity, it is related to the mean cross-sectional wetted area and tortuosity of the path through the porous media.

Because use of this method for unsaturated rocks is not well-referenced, additional confidence may be gained if the method is verified by a more direct measurement. For example, the method outlined in the YM Study Plan could be used on a few samples for verification. Another potential method of verification is the use of tomography techniques such as those used by Tidwell et al. (1997). Tomography allows for near-real-time observation of diffusion. Because the NRC will ultimately be tasked with reviewing DOE characterization of matrix diffusion in the unsaturated zone, NRC staff may wish to pursue development of such verification techniques. However, resources should only be expended in this area if DOE plans to use a matrix diffusion model for the unsaturated zone.

4.1.3 Applicability of Laboratory Measurements to Field Conditions

It is not clear whether diffusion coefficients determined in the laboratory are truly representative of field conditions because differences in temperature, pore geometry, and matrix surface alteration may result in significant differences in rates of diffusive mass transfer.

The effect of temperature on D_w, and thus D_{eff}, can be seen in the Stokes-Einstein equation

$$D_w = \frac{kT}{6\pi \mu r} \tag{4-1}$$

where k is the Boltzman constant, T is absolute temperature, μ is the temperature-dependent kinematic viscosity of water, and r is effective molecular radius of the solute. Using Eq. (4-1), it can be shown that, for any given solute, the value of D_w should approximately double due to a temperature change from 15 to 50 °C; most of this doubling effect is due to the decrease in the viscosity of water over this temperature range. Most laboratory measurements are conducted within this temperature range, typically at 25 °C. When temperature profiles of transport flow paths are not known, diffusion coefficients should be conservatively estimated using the lowest temperature the solute is likely to encounter.

Matrix porosity and pore geometry may also differ between laboratory and field conditions. The combined effect of porosity and pore geometry can be treated as a lumped parameter called a formation factor (*F*) where

$$F = \theta_{im} \frac{c}{\tau^2} . \qquad (4\text{-}2)$$

Archie (1942) suggested an empirical relationship whereby *F* varies in proportion to θ_{im}^{n}, where n has values of between 1.3 and 2.5 for various rock types. Dullien (1992) derived a physically based equation relating *F* to the range of pore throat diameters. Such relationships illustrate the important effect of porosity and pore geometry on the effective diffusion coefficient. Now, consider the fact that *in-situ* rock can be subjected to overburden pressure that could act to reduce both effective porosity and pore throat necks sizes from that encountered under laboratory conditions. Grisak et al. (1988) suggest that rates of solute diffusion through porous rock will diminish rapidly with depth due to overburden pressure; however, they provide no laboratory or field evidence for this assertion. Ohlsson and Neretnieks (1995) have also expressed concern over the fact that laboratory samples have been "de-stressed". Another matter that could influence laboratory results is the mechanical stress of sample collection and preparation which may alter pore structure or produce new fissures and result in higher diffusion rates in laboratory experiments.

It is also unclear whether results of laboratory diffusion experiments are valid when used to infer diffusion rates into natural fracture surfaces. Natural fracture surfaces have generally undergone some degree of chemical or mechanical alteration, and may be covered with a fracture coating. In their literature survey of matrix diffusion, Ohlsson and Neretnieks (1995) report that both diffusivities and sorption coefficients have been found to be the same order of magnitude or larger in most fracture coating materials compared to unaltered rock.

4.2 FIELD STUDIES

Field studies of the effects of matrix diffusion at YM discussed in this report are limited to discussions of tracer tests conducted at the C-Hole complex near YM, and the implications of bomb-pulse Chlorine-36 (^{36}Cl) found in fracture zones of the ESF.

4.2.1 C-Hole Tracer Tests

Tracer tests began at the C-Hole complex in February, 1996 and have continued intermittently until the present. The C-Hole complex consists of three wells (UE25c#1, UE25c#2, and UE25c#3), that are located approximately 2 km southeast of the proposed repository footprint. Each well penetrates about 900 m below land surface, and 500 m below the static water level (Geldon, 1996). The tracer tests discussed here were all conducted in a packed-off 90-m interval of the of the lower Bullfrog member of the Crater Flat Formation. This interval contains the most transmissive intervals in all three wells, and the high bulk-to-matrix permeability contrast is indicative of fracture-dominated flow.

Ideal tracer tests for shedding light on the issue of matrix diffusion are those performed under nearly identical conditions with the only significant difference being the diffusive properties of the tracers used in the test. One such test was initiated on October 9, 1996, and results were interpreted by Reimus and Turin (1997); a summary of their methods and interpretation follows.

Tracers used for the October 9, 1996 test were: (i) lithium ion, (ii) bromide ion, (iii) pentafluorobenzoate (PFBA), and (iv) carboxylate-modified latex polystyrene microspheres with a 0.36-μm diameter. Tracers were injected simultaneously into well c#2 and recovered from well c#3 with partial recirculation. The two wells are about 30 m apart at the surface. Bromide and PFBA served as nonsorbing solutes with free water diffusion coefficients differing by about a factor of two ($D_w \sim 1.5 \times 10^{-10}$ and 0.75×10^{-10} m^2/s, respectively). Thus, if matrix diffusion occurs, the bromide ion would be expected to diffuse more readily, and would be attenuated relative to PFBA. Conversely, if no matrix diffusion occurs, the two tracers would behave identically. The polystyrene microspheres served as large, low diffusivity tracers that should be excluded from the rock matrix and hence provide an indication of true fracture flow in the system without the effects of matrix diffusion. The lithium ion was used to investigate sorptive properties rather than diffusive properties and is not discussed further.

Tracer measurements in the recovery well show a double-peaked behavior. The PFBA and bromide responses showed qualitative evidence of matrix diffusion, as normalized concentrations are higher for PFBA at both peaks, and the second bromide peak appeared delayed relative to PFBA. These features are interpreted by Reimus and Turin (1997) to be indicative of matrix diffusion. The microsphere tracer results were ambiguous, with the only clear conclusion being that they indicate the potential for colloid transport over tens of meters with significant filtration.

The observed attenuation and delayed second peak of bromide relative to PFBA represents a small difference which may be attributed to small biases in measurement techniques. A similar test, conducted either on a larger scale or at a lower flow rate, could help to verify these preliminary interpretations of Reimus and Turin. For example, one could expect to see even greater attenuation of bromide relative to PFBA at a slower flow rate because there is more time for diffusion.

Reimus and Turin (1997) also attempted to determine diffusion properties by fitting a diffusion model to the tracer test data. Perhaps their most important conclusion in this regard is that, although it is possible to estimate an upper limit to the diffusion coefficient (constrained by the fact that the mass fraction of tracer cannot exceed 1), reasonably good fits to the data could also be obtained by assuming no matrix diffusion at all.

4.2.2 Implications of ^{36}Cl in the Exploratory Studies Facility

Elevated atmospheric ^{36}Cl occurred in the 1950s to 1960s as a result of above ground nuclear weapons testing. Elevated ^{36}Cl detected in the ESF is thought to be a result of this "bomb-pulse;" hence, the bomb-pulse ^{36}Cl must have been transported to the ESF in a time frame of less than approximately 40 yr. This bomb-pulse ^{36}Cl is generally associated with fracture zones which ostensibly represent fast flow pathways.

Actually, there is a paradox to the ^{36}Cl observations: ^{36}Cl is sampled in the ESF from matrix pore water in fractured zones, which means it somehow migrated into the matrix; on the other hand if ^{36}Cl diffuses significantly into the matrix, such rapid travel times would not be expected. This paradox can be settled by the a conceptual model of limited matrix diffusion that only occurs in relatively wet fracture zones where matrix is broken into small pieces and hence has a large surface area for diffusion.

This view of limited matrix diffusion in the unsaturated zone indicates that application of diffusion models that work in saturated laboratory studies and in saturated zone field studies are not appropriate for the unsaturated zone at YM. For example, based on laboratory-determined diffusion coefficients, chloride can diffuse tens of centimeters into rock matrix on a time scale of several months to a few years. Yet this is not observed with ^{36}Cl near fracture zones in the ESF. Additionally, episodic fast flows and capillary-driven imbibition add further uncertainty to the significance of matrix diffusion in the unsaturated zone.

4.3 EVIDENCE FOR LIMITED MATRIX DIFFUSION

It is clear from laboratory studies that significant matrix diffusion can occur in low-porosity, low-permeability rocks. Still, uncertainty remains as to whether laboratory studies are directly applicable to field conditions. In this section, several field observations are discussed that suggest a limited role of matrix diffusion

4.3.1 Unsaturated Zone

As already discussed, ^{36}Cl data from the ESF provided evidence for limited matrix diffusion in the unsaturated zone. This argument against matrix diffusion in the unsaturated zone is strengthened by White et al. (1980) and Murphy and Pabalan (1994), who point out significant differences between the geochemical signatures of fracture water and matrix pore water in the unsaturated zones near YM and at Rainier Mesa. Murphy and Pabalan also pointed out similarities between fracture water at Rainier Mesa, and YM saturated zone water. Yang et al. (1996) presented YM data showing marked differences in the geochemical signatures of unsaturated zone pore waters and saturated zone well water, and similarities between perched zone water at YM and saturated zone water.

In addition to geochemical evidence, natural analog studies have been used to suggest limited matrix diffusion in the unsaturated zone. For example, investigations of the Nopal I uranium deposit (Pearcy et al., 1995) in the Peña Blanca mining district of Mexico revealed that occurrence of uranium in unfractured tuff matrix was limited to distances less than 1 mm from uranium enriched fracture filling minerals. Many other natural analog studies suggest limited matrix diffusion: for example, Ohlsson and Nerenieks (1995), after reviewing several natural analog studies, concluded that matrix diffusion seems to be limited to weathered or altered zones. One problem with natural analog studies, however, is that unknown initial and boundary conditions, as well as other possible transport mechanisms (e.g., imbibition, evaporation), make it difficult to draw unambiguous conclusions regarding matrix diffusion.

4.3.2 Saturated Zone

Murphy (1995) pointed out the common occurrence of calcite in rocks below the water table in the vicinity of YM, and the fact that saturated zone water at YM is undersaturated with respect to calcite. These observations are an indication that groundwater flow is channelized and that portions of rock that contain calcite are effectively isolated from present water circulation. Murphy (1995) also suggested that the presence of undissolved calcite and undersaturated water implies that matrix diffusion between channelized groundwater and rock matrix water is limited, perhaps over time scales of millions

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of years. However, this conclusion may be premature, because no serious attempt has been made to estimate time scales for dissolution of calcite minerals from rock matrix by diffusion alone. It is possible that solute transport by matrix diffusion could occur rapidly enough to warrant inclusion into PA models, yet be too slow to dissolve calcite locked deep within matrix blocks—even over millions of years. It is therefore recommended that modeling be conducted to assess whether the observations pointed out by Murphy (1995) can be used to infer limited matrix diffusion in the saturated zone.

Geochemical data of the type used as evidence against matrix diffusion in the unsaturated zone would be useful for determining the potential for matrix diffusion in the saturated zone. Unfortunately, there is a lack of geochemical data for rock matrix pore water in the saturated zone.

5 NEEDS FOR FURTHER TESTING

Although much is known about the process of matrix diffusion in rocks at YM, there is still a considerable amount of uncertainty regarding the impact this process might have on overall repository performance. Much of this uncertainty lies in our understanding of matrix diffusion in the unsaturated zone. Although matrix diffusion in saturated zones is well understood, the ability to abstract matrix diffusion into PA models is limited by the lack of knowledge regarding preferential flow pathways and flow system geometry. In this section, areas of research that could improve our ability to develop an effective PA abstraction of the matrix diffusion process are discussed. Discussion is focused on laboratory studies, field testing, and transport modeling. It should be noted that no in depth scoping analyses have been performed to evaluate the feasibility or the utility of the following proposals; the intent of this discussion is merely to identify potential research areas for further discussion.

5.1 LABORATORY STUDIES

The electrical conductivity methods proposed by Triay et al. (1996), discussed in section 4.1.1, could provide significant insight into matrix diffusion in unsaturated rock. However, because this proposed method is an indirect measurement of diffusion properties, confidence in results could be improved by conducting some additional experiments for verification of results. Such additional experiments might include:

- Use of tomography methods to visualize migration of brine solution into unsaturated rock matrix (e.g., Tidwell et al., 1997)

- Conducting electrical conductivity measurements during wetting and drying cycles to examine the possibility of hysteretic diffusion properties

Although matrix diffusion under saturated conditions is fairly well understood, a few mysteries still exist. For example, diffusion of sorbing cations in the rock beaker experiments of Triay et al. (1996) occurred much more rapidly than expected. It is unclear whether this is a commonly observed phenomenon; however, if this observation could be attributed to some physical process, it could bode well for PA predictions of repository performance. An additional area of uncertainty in saturated matrix diffusion is the effect of overburden pressure on pore geometry and, hence, on diffusion. A laboratory experiment that might be helpful in this regard is measurement of the electrical conductivity response to stress on a saturated rock sample.

5.2 FIELD TESTING

Ongoing tracer studies at the C-Hole complex are expected to continue to shedding light on the process of matrix diffusion in the saturated zone beneath YM. The CNWRA and the NRC are currently conducting independent interpretations of these C-Hole tests. Tracer tests conducted over greater distances would prove useful for verifying the encouraging—though not conclusive—results of earlier tracer studies. Tracer tests over greater distances could improve the ability to observe matrix diffusion in two ways. First, the time scale would increase, allowing more time for solutes to diffuse. Second, when the scale of the tracer tests is greater than the scale of heterogeneities, the approximation of a homogeneous continuum is less likely to bias results.

A major obstacle to effective interpretation of tracer tests is a lack of understanding of the flow geometry in the saturated zone beneath YM. Because the matrix diffusion transport model is sensitive to the spacing between the fracture-dominated preferential flow paths, additional characterization in this regard would prove extremely useful to both tracer test interpretation and abstraction of matrix diffusion into PA models. Because resources available for drilling of additional boreholes are limited, innovative approaches are needed in order to obtain a better understanding of the YM groundwater flow system. Data and core samples from existing boreholes may hold clues that are as yet undiscovered. For example, as Murphy (1995) pointed out, the existence of undissolved calcite in saturated zone rock matrix is evidence for the existence of channelized groundwater flow. If so, then an analysis of the spacial distribution of such undissolved calcite from existing boreholes may help to place bounds on the likely spacing between preferential flow paths.

5.3 TRANSPORT MODELING

Additional transport modeling is recommended to gain a better understanding of the mechanisms that are important for consideration in future PA codes. Modeling studies could prove useful in the following ways.

- The importance of considering multiple rates of diffusion that occur within rock matrix could be evaluated.

- Various conceptual models for flow geometries and patterns could be tested. For example, it would be useful to compare results from the following scenarios: flow in narrow, highly fractured zones bounded by relatively unfractured rock (e.g., faults); flow that occurs in many discrete finger-type pathways; and flow that is relatively uniform.

- Results from matrix diffusion transport models could be compared to results from first-order-kinetic transport models. This would be useful in evaluating the reasonableness of using the first-order-kinetic model that is already incorporated into NEFTRAN II.

- A matrix diffusion transport model could be developed for the unsaturated zone in an attempt to identify unsaturated flow regimes that are consistent with observed bomb-pulse ^{36}Cl in the ESF.

- Modeling of time scales for dissolution of calcite minerals in the YM saturated zone should be performed to evaluate if their presence in waters that are undersaturated with calcite is an indication of limited matrix diffusion.

6 CONCLUSIONS

Previous PA models for YM relied on dual-permeability approaches to account for dilution of migrating solutes by interaction with near-stagnant water in adjacent rock matrix. The ability to abstract the process of matrix diffusion into PA models could provide a significant improvement over these dual-permeability approaches, which lack a sound physical basis.

Scoping calculations performed in this report indicate that the assumption of interacting mobile and immobile solute transport domains is reasonable for saturated, low-permeability, fractured tuffs at YM. Sensitivity analyses reveal that matrix diffusion models are strongly affected by the value of the effective matrix block size, the effective diffusion coefficient, the retardation coefficient for the assumed mobile and immobile regions, the fluid flux through the system, the total porosity, and the length scale under consideration. These sensitivity analyses also demonstrate that the conventional concept of retardation factors is not appropriate for predicting solute transport times when matrix diffusion occurs.

Evidence of limited matrix diffusion in the unsaturated zone suggests that conventional matrix diffusion models are not appropriate for unsaturated zone radionuclide transport. Additional laboratory work and modeling may help to gain insight into the possibility for radionuclide transport in the unsaturated zone. At present, however, the conservative approach is to treat matrix and fractures as separate and noninteracting.

Much more is known about saturated zone matrix diffusion processes. Results from field tracer studies—though not conclusive—lend support to the possibility of radionuclide attenuation due to matrix diffusion. Based on numerous laboratory investigations, there can be little doubt that matrix diffusion does indeed occur, however it is uncertain that it has any significant impact on radionuclide migration at YM. Although the impact of matrix diffusion is minor on the scale of tracer tests, the impact could be quite significant over the scale of several kilometers used in PA models.

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ANALYTICAL SOLUTION USE FOR SENSITIVITY ANALYSES

APPENDIX A

The analytical solution for a two-region (dual-porosity) model with 1D advective and dispersive transport through evenly spaced parallel fractures with diffusive mass transfer into rock matrix was derived by van Genuchten (1985), based on earlier work by Rasmuson and Neretnieks (1980) who derived a similar solution for spherical aggregates. To predict effluent (breakthrough) curves for a finite system the following solution for the flux-averaged concentration (C_e) should be used:

$$C_e(\mathrm{T}) = \frac{1}{2} + \frac{2}{\pi} \int_0^{\infty} \exp\left(\frac{P}{2} - \mathrm{z_p}\right) \sin\left(2\gamma\lambda^2\mathrm{T} - \mathrm{z_m}\right) \frac{d\lambda}{\lambda} \; . \qquad \text{(A-1)}$$

Here, λ is a dummy variable of integration, T is dimensionless time, given by

$$\mathrm{T} = \frac{qt}{\theta L} \; ; \qquad \text{(A-2)}$$

and $\mathrm{z_p}$ and $\mathrm{z_m}$ are given by the following equations:

$$\mathrm{z_p} = \left[\frac{1}{2}\left(\mathrm{r_p} + \Omega_1\right)\right]^{\frac{1}{2}} \qquad \text{(A-3)}$$

$$\mathrm{z_m} = \left[\frac{1}{2}\left(\mathrm{r_p} - \Omega_1\right)\right]^{\frac{1}{2}} \qquad \text{(A-4)}$$

$$\mathrm{r_p} = \left(\Omega_1^{\,2} + \Omega_2^{\,2}\right)^{\frac{1}{2}} \qquad \text{(A-5)}$$

$$\Omega_1 = \frac{P^2}{4} + \gamma P(1-\beta)R\Psi_1 \qquad \text{(A-6)}$$

$$\Omega_2 = 2\gamma P\beta R\lambda^2 + \gamma P(1-\beta)R\Psi_2 \qquad \text{(A-7)}$$

$$\Psi_1 = \frac{3\lambda(\sinh 2\lambda + \sin 2\lambda)}{\cosh 2\lambda - \sin 2\lambda} - 3 \tag{A-8}$$

$$\Psi_2 = \frac{3\lambda(\sinh 2\lambda - \sin 2\lambda)}{\cosh 2\lambda - \cos 2\lambda} . \tag{A-9}$$

The parameters γ, β, θ, P, R, q, t, and L are defined in section 3.2 and 3.3 of this report.