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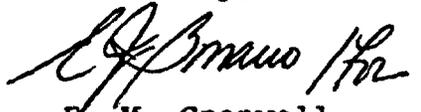
Mr. Walton Kelly
U.S. Nuclear Regulatory Commission
Mail Stop 623-SS
Washington, DC 20555

Dear Mr. Kelly:

Enclosed is the monthly report for FIN A-1756, Geochemical Sensitivity Analysis for August 1985.

Please feel free to contact me if you have any questions or comments.

Sincerely,



R. M. Cranwell
Supervisor
Waste Management Systems
Division 6431

RMC:6431:jm

Enclosure

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August 14, 1985

Copy to:

Office of the Director, NMSS
Attn: Program Support Staff
Robert Browning, Director
Division of Waste Management
Malcolm R. Knapp
Division of Waste Management
Kenneth Jackson
Division of Waste Management
Office of Research, NRC
Document Control Center,
Division of Waste Management
6400 R. C. Cochrell
6430 N. R. Ortiz
6431 R. M. Cranwell
6431 M. D. Siegel
1500 W. Herrmann
1510 J. W. Nunziato
1512 J. C. Cummings
1512 K. L. Erickson

PROGRAM: Geochemical Sensitivity Analysis FIN#: A-1756

CONTRACTOR: Sandia National Laboratories BUDGET PERIOD: 10/01/84 - 9/30/85

DRA PROGRAM MANAGER: W. R. Kelly BUDGET AMOUNT: 235K

CONTRACT PROGRAM MANAGER: R. M. Cranwell FTS PHONE: 844-8368

PRINCIPAL INVESTIGATOR: M. D. Siegel FTS PHONE: 846-5448

PROJECT OBJECTIVES

The objective of this project is to provide technical assistance to the NRC in determining the sensitivity of far-field performance assessment calculations to uncertainties in geochemical and hydrological input data and in the representation of geochemical processes in transport models. In Task I, the error in model calculations of integrated radionuclide discharge due to speciation, kinetic and sorption effects will be evaluated. In Task II, the potential importance of organic molecules and colloids will be examined. SNLA will assist the NRC in determining how geochemical processes should be represented in transport models under Task III. Short-term technical assistance will be carried out under Task IV.

ACTIVITIES DURING AUGUST 1985

Task I Uncertainty in Integrated Radionuclide Discharge

Subtask IA. Speciation Effects
(M. Siegel, R. Guzowski, S. Phillips)

A draft of a report on the uncertainties in speciation/solubility calculations related to the use of the Davies, Debye-Huckel, and Pitzer equations is in preparation. A report concerning the propagation of error in speciation calculations is also being prepared.

A review of various approaches and requirements for compilation of an internally-consistent thermochemical data base is underway. As discussed in attachments to the July monthly progress report, the level of effort for data base compilation authorized under A-1756 will not allow preparation of an internally-consistent data base. Data from other critical compilations will be incorporated into the LBL/NRC/SNLA data

base and some residual inconsistencies may remain. Currently, an effort is being made to examine alternative methods to eliminate or to assess the significance of these inconsistencies.

Synthesis of hydrogeologic data for a conceptual model for a basalt repository site was essentially completed during August.

Subtask 1B. Sorption Effects
(M. Siegel, J. O. Leckie, D. Kent, E. Shepherd)

The bulk of the effort in A-1756 during August was directed toward making modifications to the computer code MINEQL to enable Sandia staff to run the code on the SNLA CDC computer. Required modifications to the preprocessor MININP were also made. The latter program is an interactive code which helps the user to prepare input decks for MINEQL. Sample problems are currently being run to test the modified codes on the Sandia computer system. Demonstration problems and a short tutorial on the Stanford Generalized Model for Adsorption (SGMA) are being prepared for the upcoming visit of the NRC project manager.

Subtask 1C and 1D. Kinetic and Dynamic Effects

The paper, "Geochemical Sensitivity Analysis . . . Speciation and Matrix Diffusion," described in the July progress report, was submitted for publication and is appended as Attachment 1.

A revised abstract, "Approximate Methods to Calculate Radionuclide Discharge . . . Fractured Rock" was submitted for presentation and publication at the Waste Management '86 conference which will be held in March 1986. A copy of the summary is appended as Attachment 2.

Task II. Evaluation of Error Due to Organics and Colloids

No activity in August 1985.

Task IV. Short Term Technical Assistance

No activity in August 1985.

**GEOCHEMICAL SENSITIVITY ANALYSIS FOR PERFORMANCE
ASSESSMENT OF HLW REPOSITORIES: EFFECTS OF SPECIATION
AND MATRIX DIFFUSION***

M. D. Siegel and K. L. Erickson, Sandia National Laboratories, Albuquerque, NM 87185

ABSTRACT

Performance assessment requires calculating radionuclide discharge for many sets of conditions and scenarios. In general, such calculations use empirical retardation factors that describe the average effect of all radionuclide/fluid/rock interactions. This method, however, may underestimate radionuclide discharges and disguise potential violations of regulatory standards. An alternative approach, coupled reaction-transport models, can be used to obtain a detailed understanding of physicochemical phenomena but the general application of such rigorous models may be impractical in repository performance assessment.

The objective of this geochemical sensitivity analysis is to use simple, approximate models to calculate upper bounds for radionuclide discharges and to identify physicochemical conditions where more rigorous theoretical transport calculations must be done. An approximate model is given for bounding discharges of radionuclides in porous rock in scenarios where radioactive production is negligible but decay is appreciable, and several nuclides of an element migrate and undergo a speciation reaction. The model is incorporated into a methodology to determine critical combinations of hydrological and chemical parameter values that result in discharges that violate the HLW standard proposed by the U.S. Environmental Protection Agency (40CFR 191). As an example, the methodology is applied to the discharges of ^{243}Am and ^{237}Np from a reference repository. It also is shown how results from the sensitivity analyses can be used to develop criteria for designing laboratory experiments so that effects of significant speciation reactions will be detected. Approximate methods for calculating radionuclide discharge are given for extending these analyses to transport in fractured rock where diffusion of radionuclides into the matrix may occur.

INTRODUCTION

Geochemical interactions between radionuclides and rocks are but one of several barriers to the transport of radioactive waste from proposed HLW repositories. Performance assessment calculations consider the roles of the waste package, engineered facility and hydrogeochemistry of the repository site in limiting potential releases of radioactivity. The overall objective of geochemical sensitivity analysis is to assess the relative contribution of

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the uncertainty in geochemical data and models to the overall uncertainty in the predicted performance of candidate HLW repositories.

In the past, performance assessment calculations¹⁻³ have used simple models to represent complex geochemical processes. In particular, solute-water-rock interactions have been represented with retardation factors calculated from empirical sorption ratios (K_d , R_d , or R_s)^{4,5} obtained under conditions which simulate the range of environments predicted to prevail at specific repository sites. Figure 1 illustrates the general structure of calculations carried out at Sandia National Laboratories to assess compliance of hypothetical HLW sites with the proposed EPA Standard 40CFR Part 191.⁶ More detailed discussions of these calculations can be found in References 1-3. In these calculations the discharge of radionuclides at the accessible environment is calculated over a ten thousand year period. The use of simple algorithms to represent geochemical processes has been justified in part by the complexity of the calculation of integrated discharge for solutes which are affected by radioactive decay and production. In addition, statistical sampling of model input parameters⁷ and a large number of calculations are required to represent the uncertainties in possible hydrogeologic and geochemical conditions at the candidate HLW sites.^{8,9}

The adequacy of the use of simple retardation factors and sorption ratios in calculations of radionuclide discharge and the utility of the large amount of sorption data that have been collected by the Department of Energy and its contractors have been questioned by a number of researchers.¹⁰⁻¹² In general, the speciation of the radioelements in the sorption experiments is not known and sorption behavior cannot be confidently predicted for conditions that differ from those of the experiments. Radionuclides are not introduced into the experimental solutions in the forms that would be released from the nuclear waste, and the relatively short duration of the experiments may preclude detection of any slow speciation reactions that could change sorption behavior and lead to increased radionuclide discharge.¹³

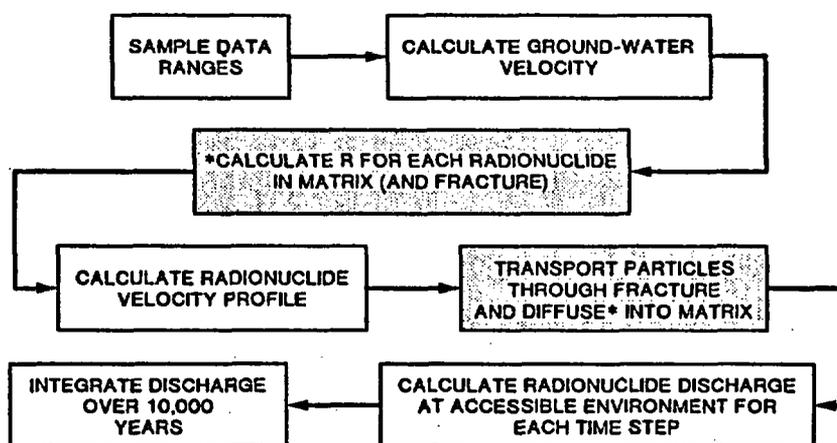


Figure 1. Simplified Outline of Performance Assessment Calculations. Shaded areas indicate steps in which geochemical processes are considered.

Coupled reaction-transport models which explicitly model geochemical reactions have been proposed as an alternative to currently available performance assessment models.^{11,14} The use of such models has been hampered in part by the lack of fundamental thermochemical data describing surface complexation reactions and by difficulties in extrapolating theoretical models of the sorption of trace metals by simple oxides and aluminosilicates to the behavior of natural materials.^{15,16} In addition, the high computing costs associated with realistic calculations of radionuclide discharge over a 10 km distance and 10,000 year period, at present, preclude the use of such models in repository performance assessment. For example, it has been estimated that a single calculation using the code TRANQL¹⁷ for a relatively geochemically simple system would cost more than \$20,000.¹⁶ The calculation examined involved 14 aqueous species of a single element, one-dimensional transport in a monomineralic column, and did not consider radioactive decay or production. For comparison, a calculation using the computer code NWFT/DVM⁹ which considers transport of 10 elements of a radioactive decay chain through a column consisting of several layers of minerals with contrasting sorptive capacities costs less than \$50.¹⁸ This code, however, represents geochemical interactions with a simple retardation factor as illustrated in Figure 1 and is subject to the criticisms described above.

Coupled reaction-flow models such as TRANQL are clearly useful in providing basic mechanistic insights and identifying key chemical parameters in radionuclide transport. However, as illustrated above, the routine use of such codes in performance assessment is impractical. The objective of the geochemical sensitivity analysis described below is to identify physicochemical conditions under which the use of such complex codes is truly required in order to assess compliance of candidate HLW repositories with the EPA Standard 40CFR 191. In this analysis, a general model is given for bounding radionuclide discharge in scenarios where radioactive production is negligible, but decay is appreciable; several nuclides of a radioelement are present, and a speciation reaction occurs during transport. The model is incorporated into a methodology for determining critical combinations of hydrologic and geochemical parameter values that result in discharges that violate the EPA Standard. As an example, the methodology is applied to releases of ²³⁷Np and ²⁴³Am from a reference repository. It is shown that the results of the analysis can be used to develop criteria for designing laboratory experiments so that significant speciation reactions will be detected. The analysis is developed initially for porous media. Hydrological and chemical criteria are also derived for application of the methodology to fractured media.

THEORY

General Transport Model

In general, transport of radionuclides involved in any number of homogeneous and heterogeneous chemical reactions is described by equations of the form:

$$\left\{ \begin{array}{c} \text{rate} \\ \text{of} \\ \text{accumulation} \end{array} \right\} = \left\{ \begin{array}{c} \text{net rate of} \\ \text{influx by} \\ \text{convection} \end{array} \right\} + \left\{ \begin{array}{c} \text{net rate of} \\ \text{influx by} \\ \text{dispersion} \end{array} \right\} \\
- \left\{ \begin{array}{c} \text{rate of} \\ \text{radioactive} \\ \text{decay} \end{array} \right\} + \left\{ \begin{array}{c} \text{rate of} \\ \text{radioactive} \\ \text{production} \end{array} \right\} \quad (1) \\
+ \left\{ \begin{array}{c} \text{net rate of} \\ \text{production} \\ \text{by heterogeneous} \\ \text{reactions} \end{array} \right\} + \left\{ \begin{array}{c} \text{net rate of} \\ \text{production} \\ \text{by homogeneous} \\ \text{reactions} \end{array} \right\} ,$$

where a separate equation is written for each species of each radionuclide.

The objective of this analysis is to derive simple analytical expressions from the comprehensive transport Equation (1) which will yield conservative estimates of integrated radionuclide discharge. These expressions can be used for parametric sensitivity analyses or can be used to formulate more accurate retardation factors for use in performance assessment calculations.

The first five terms on the right hand side of the above expression are normally included in solute transport models. The fifth term is generally used to represent reversible first-order sorption reactions (adsorption and ion exchange). Similar terms also could be used to calculate upper bounds on radionuclide discharge when colloid retention and irreversible sorption must be considered.

The last term in the above expression represents reactions between dissolved constituents. These may include changes in radionuclide speciation, precipitation by homogeneous nucleation, and colloid formation. As discussed later for the purpose of calculating upper bounds to radionuclide discharge, these reactions can be represented by expressions of the form:

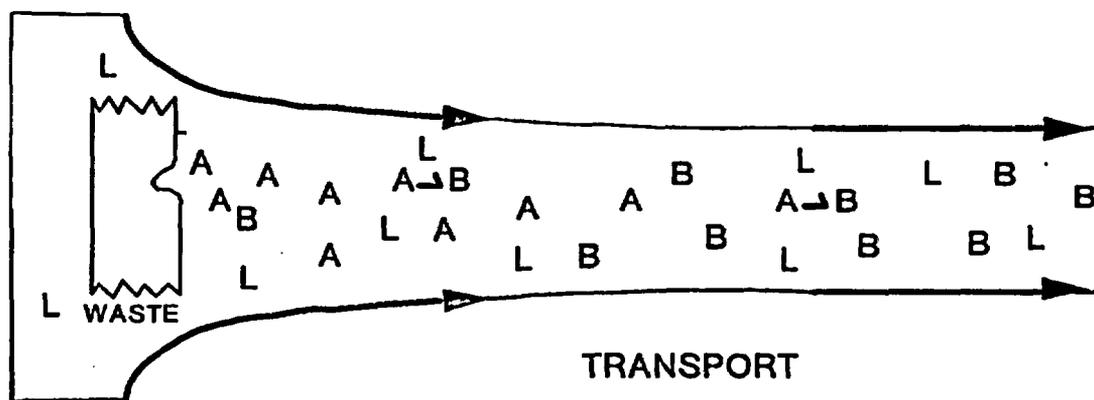
$$\left\{ \begin{array}{c} \text{net rate of} \\ \text{production by} \\ \text{homogeneous} \\ \text{reactions} \end{array} \right\} = \sum_n k_n C_i \quad (2)$$

where k_n is the rate constant for the n^{th} reaction involving the i^{th} species of the radionuclide and C_i is the species concentration.

The proposed EPA Standard 40CFR 191⁶ regulates the integrated discharge of radionuclides from a HLW repository to the accessible environment. Critical combinations of values of geochemical and hydrologic parameters which violate the EPA Standard can be identified in the following manner:

1. Terms for both homogeneous and heterogeneous reactions are incorporated into the radionuclide transport equation for each species;
2. The equations are simplified, using conservative assumptions which calculate an upper bound to radionuclide discharge, and are solved.
3. The integrated discharge is calculated for the 10,000-year regulatory period; the discharges of all chemical species of a radionuclide are summed and the resultant expression is set equal to the EPA radionuclide release limit W ;
4. The resulting equation is solved numerically to determine combinations of the parameters which cause violations of the EPA Standard.

This method of sensitivity analysis can best be illustrated by its application to a specific scenario. For this paper, a scenario is chosen in which radionuclide discharges are greater than those predicted by calculations which do not include the effects of speciation reactions. Figure 2 depicts the release of a radionuclide as an unstable sorbing species A which transforms to a mobile species B during transport. Such a transformation could occur due to kinetic constraints (i.e., the metastable species A is released easily from the waste form due to steric factors but is unstable in the solutions in the repository near-field) or due to changes in the geochemical conditions. Clearly, the total integrated discharge of the radionuclide as species A and B will be greater than that predicted by calculations of the discharge which assume that all the nuclide is released as species A. The magnitude of the error will depend upon the relative mobilities of species A and B as well as the rate of the transformation $A \rightarrow B$.



DEFINITIONS

A : SORBING AQUEOUS SPECIES [eg - UO_2^{2+} , $(UO_2)_3(OH)_5^+$]

B : NON-SORBING AQUEOUS SPECIES [eg. $UO_2(CO_3)_3^{4-}$]

L : GROUND-WATER LIGAND [eg HCO_3^-]

k : RATE CONSTANT FOR REACTION $A + L \rightarrow B$

Figure 2. A Scenario for Geochemical Sensitivity Analysis. Species A is a hypothetical sorbing species which has been studied in sorption experiments. The sensitivity of radionuclide discharge to the production of another species B is examined in this study.

Step 1: Formulate General Transport Equation

The reaction rate expressions for this scenario are:

$$-\frac{dC}{dt} = k_1 C_A^x C_L^z - k_2 C_B^y = \frac{1}{b} \frac{dC}{dt} \quad (3)$$

where C denotes concentration; k_1 and k_2 denote forward and reverse reaction rate constants, respectively; t denotes time, and the exponents x, y, and z are usually positive integers.

Simultaneously, species A and B can be involved in heterogeneous reactions with the rock matrix. In this analysis, such reactions are restricted to sorption phenomena, and local sorption equilibrium between matrix and pore water is assumed. Under these conditions, the material balance for species A can be written:

$$\begin{aligned} \frac{\partial C}{\partial t} = & -v \cdot \nabla C_A + \nabla \cdot D \nabla C_A - \lambda \cdot \left(C_A + (\rho^*/\phi) F_A(C_A, pH, T \dots) \right) \\ & - (\partial C_A / \partial t) \cdot (\rho^*/\phi) \partial F_A(C_A, pH, T \dots) / \partial C_A \\ & - k_1 C_A^x C_L^z - k_2 C_B^y + P_A \end{aligned} \quad (4a)$$

and the material balance for species B can be written:

$$\begin{aligned} \frac{\partial C}{\partial t} = & -v \cdot \nabla C_B + \nabla \cdot D \nabla C_B - \lambda \cdot \left(C_B + (\rho^*/\phi) F_B(C_B, pH, T \dots) \right) \\ & - (\partial C_B / \partial t) (\rho^*/\phi) \partial F_B(C_B, T, pH \dots) / \partial C_B \\ & + b \left(k_1 C_A^x C_L^z - k_2 C_B^y \right) + P_B \end{aligned} \quad (4b)$$

Here, \vec{v} is the interstitial velocity; D the dispersion coefficient; λ the radionuclide decay constant; P the rate of radioactive production; ϕ the matrix porosity; and ρ^* the bulk density of the rock. $F_A(C_A, pH, T \dots)$ is the concentration of species A associated with the matrix as described by the sorption equilibrium isotherm. It is generally a function of C_A , temperature (T), and solution composition.

Step 2: Formulate and Solve Simplified Expressions for Bounding Radionuclide Discharge

Equations 4a and 4b can be approximated by simpler expressions that will give upper bounds to integrated radionuclide discharge. A detailed discussion of the approximation is given in Reference 20. The terms for chemical reaction rate and sorption are simplified as follows.

• Reaction Rate

If the exponents x , y , and z in Equation 4 are unity or greater and if C_A is less than 1 molar, then the rate expression

$$-dC_A/dt = k^*C_A = (1/b)dC_B/dt \quad (5)$$

will give reaction rates and radionuclide discharges equal to or greater than those obtained from Equation 3. Here, $k^* = k_1 C_{Lmax}^z$, where C_{Lmax} is the maximum possible value of C_L .

• Sorption Equilibria

Sorption ratios (Rd , Kd , or Rs) can be defined as

$$Rd_A \equiv \frac{F_A(C_A, T, pH \dots)}{C_A} \quad \text{and} \quad Rd_B \equiv \frac{F_B(C_B, T, pH \dots)}{C_B}$$

Often, solution-phase concentrations will be sufficiently dilute, and the temperature, solution-phase pH, and ionic strength sufficiently constant so that the sorption isotherms for species A and B are at least approximately linear. This means that $Rd_A \approx$ a constant $\approx \partial F_A / \partial C_A$ and $Rd_B \approx$ a constant $\approx \partial F_B / \partial C_B$. If the sorption ratios are not constants, minimum values can be determined which will yield predicted cumulative radionuclide discharges that are greater than those obtained using the more exact expressions for sorption equilibria.

• Radioactive Production

Many of the isotopes important to high-level waste disposal are not produced by radioactive processes in significant quantities during the 10,000-year period regulated by the EPA standard.²⁰

Consideration of initial inventories and half-lives of radionuclides can lead to a number of simplifying assumptions in speciation and transport calculations for different radioelements in different scenarios. In a previous report,¹³ radioactive production and decay of neptunium-237 could be ignored in an analysis of discharge of this radionuclide after a 1000-year isolation period. In this report radioactive decay is considered; however, consideration of radioactive production will be deferred until a later work.

• 1-D Equation

For purposes of bounding cumulative radionuclide discharges under most conditions, Equations 4a and 4b can be reduced to one spatial dimension with no dispersion when the mean radionuclide residence time is much less than the regulatory period. (See Reference 20). The material balances, Equations 4a and 4b, then can be reduced to

$$\frac{\partial C_A}{\partial t} + \frac{v}{R_A} \frac{\partial C_A}{\partial x} + \lambda C_A + \frac{k^*}{R_A} C_A = 0 \quad (6a)$$

and

$$\frac{\partial C_B}{\partial t} + \frac{v}{R_B} \frac{\partial C_B}{\partial x} + \lambda C_B - \frac{bk^*}{R_B} C_A = 0 \quad (6b)$$

where $R_A = 1 + (\rho^*/\phi)Rd_A^*$, and $R_B = 1 + (\rho^*/\phi)Rd_B^*$,

and Rd_A^* and Rd_B^* are the sorption ratios corresponding to linear isotherms or appropriate values for bounding cumulative radionuclide discharges. For the case in which radionuclide release from the repository is solubility limited, initial and boundary conditions for Equation 6a are

$$C_A(x,0) = 0 \text{ and } C_A(0,t) = C_A^0$$

and for Equation 6b

$$C_B(x,0) = 0 \text{ and } C_B(0,t) = C_B^0$$

For purposes of illustration let $b = 1$. Equations 6a and 6b with the above initial and boundary conditions can be solved using the method of Laplace transforms,

$$C_A = C_A^0 \exp[-(\lambda R_A + k^*)x/v] H(t - R_A x/v) \quad (7a)$$

and

$$C_B = C_B^0 \exp(-\lambda R_B x/v) H(t - R_B x/v) + \Gamma_B \left\{ 1 - \exp[-\alpha(t - R_B x/v)] \right\} H(t - R_B x/v) - \Gamma_A \left\{ 1 - \exp[-\alpha(t - R_A x/v)] \right\} H(t - R_A x/v) \quad (7b)$$

where $H(t) = \begin{cases} 0 & t < 0 \\ 1 & t > 0 \end{cases}$

$$\alpha = \frac{(R_A - R_B)\lambda + k^*}{R_A - R_B}$$

$$\Gamma_A = \frac{k^* C_A^0}{(R_A - R_B)\lambda + k^*} \exp[-(\lambda R_A + k^*)x/v]$$

$$\Gamma_B = \frac{k^* C_A^0}{(R_A - R_B)\lambda + k^*} \exp(-\lambda R_B x/v)$$

• Systems of Multiple Radionuclides

Equations 7a and 7b rigorously apply to a system in which a single radionuclide exists for the element of interest, and only two chemical species are present. If several radionuclides of the element were present, sorption equilibria and chemical reaction rates would be functions of the total concentration of the element. The transport equations for the radionuclides would be coupled and require simultaneous solution. However, to bound cumulative radionuclide discharges the transport equations can be uncoupled, as shown in Reference 20 and solved independently, provided that reaction rates and sorption equilibria do not differ appreciably between nuclides. The uncoupled equations would be of the same form as Equations 7a and 7b.

• Transport in Fractured Media

Equations 7a and 7b rigorously apply only to transport in a porous medium in which sorption equilibrium between the fluid and bulk rock exists. Several

of the potential HLW repository sites are in fractured media where fluid flow is primarily in the fractures. In these rocks, the time required for radionuclide diffusion into the rock matrix must be considered in transport calculations.

Approximate methods for calculating radionuclide discharges in fractured, porous rock can be derived from a set of rigorous general transport equations.^{22,23} When the relaxation times for concentration perturbations in the porous matrix are small relative to the radionuclide residence time, then the fracture fluid and the porous matrix are locally near equilibrium (or more generally, a quasi-steady-state is approached with respect to radionuclide diffusion). Under these conditions, transport in the fractured medium can be represented by a porous medium approximation.

In order to identify these conditions, three approximate methods for calculating radionuclide discharges in fractured, porous rock have been evaluated: (1) the porous medium approximation where radionuclide diffusion rates into the matrix are proportional to depletion rates in the fracture fluids; (2) a linear-driving-force approximation where radionuclide diffusion rates into the matrix are proportional to the difference between bulk concentrations in the matrix and the fracture fluids, and (3) a semi-infinite-medium approximation where radionuclide diffusion rates into the matrix are calculated assuming a semi-infinite matrix. The above three methods are described, criteria for application of each given, and the respective uncertainties in calculated cumulative radionuclide discharges are assessed in References 23 and 24. The criteria for application of each method were derived from a general consideration of fluid residence times in the fractures and relaxation times for radionuclide concentration gradients in the matrix. The same criteria were then obtained from the solution to the transport equations for specific cases involving radionuclide decay, chemical reaction, and varying matrix properties. For example, if fluid flow in saturated rock is one-dimensional and primarily occurs in parallel fractures having relatively uniform aperture $2b$ and spacing $2B$, and if matrix porosity ϕ_m , grain density ρ_s , fracture porosity ϕ_f , and sorption isotherms $F(C)$ in the matrix are relatively uniform, then the porous medium approximation applies when

$$x/v > 50 B^2 \alpha^2 \phi_f / \phi_m D(1-\phi_f) \quad (8)$$

The linear-driving-force applies when

$$x/v > 0.2 B^2 \alpha^2 \phi_f / \phi_m D(1-\phi_f) \quad (9)$$

and the semi-infinite medium applies when

$$x/v < B^2 \alpha^2 \phi_f / \phi_m D(1-\phi_f) \quad (10)$$

Here, D is the radionuclide diffusion coefficient in the pore water; v is the average fluid velocity in the fractures; x is the radionuclide transport path length, and α is a tortuosity/constructivity factor for the matrix.

Site-specific data for tuff and granite^{2,23-27} were used with the above criteria. Results are shown in Figure 3. For tuff, the porous medium approximation will be applicable even for relatively thin beds ($x = 30\text{m}$). The linear-driving-force or semi-infinite-medium approaches would be necessary for extreme cases involving relatively unrealistic porosities and fluid velocities. For granite, the semi-infinite medium or linear-driving-force approaches may be required, while the porous medium approximation may be applicable only to relatively large granitic bodies.

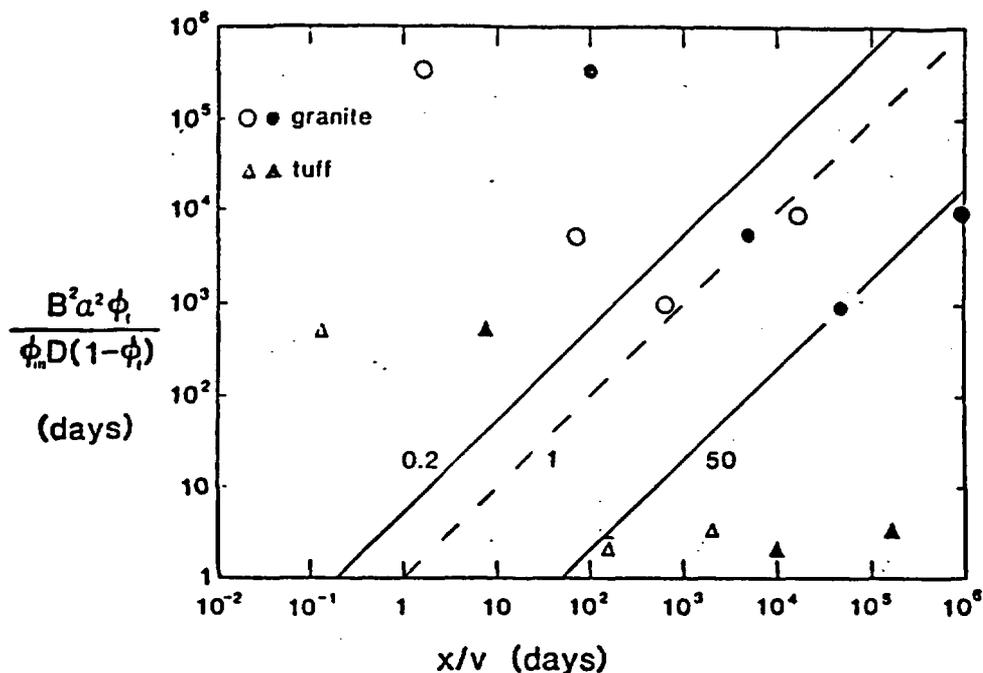


Figure 3. Application of Criteria to Representative Site-Specific Data for Granite and Tuff. Numbers on lines are ratios of $B^2 \alpha^2 \phi_f / \phi_m D (1 - \phi_f)$ to x/v . Areas below lines marked '0.2' and '50' correspond to conditions under which linear-driving-force and porous medium approximations, respectively, apply. The semi-infinite-medium approach applies in the area above the line marked '1'. Solid and open symbols refer to transport distances of $x = 2000$ meters and $x = 30$ meters respectively.

Step 3: Integrate Equations for Integrated Discharge and Sum over Species

The sum of the integrated discharges of species A and B is now set to a specified release limit for the radionuclide of interest.

$$Q \int_{t_0}^{t=10,000 \text{ yr}} (C_A + C_B) dt = f(x/v, R_A, R_B, k^*, \lambda, t_0, C_A^0, C_B^0, t^*) \leq W \quad (11)$$

where t_0 is the initial containment period; Q is the annual volumetric flux of ground water through the engineered facility; W is the release limit; $t^* = 10,000 - t_0$; λ is the radioactive decay constant; C_A^0 and C_B^0 are concentrations of species A and B in the repository, and the other terms have been defined previously.

For $R_A x/v > R_B x/v > t^*$, C_A and C_B at the accessible environment should be negligible, and Equation 12 is satisfied.

For $R_B x/v < t^* < R_A x/v$, $C_A = 0$ at the accessible environment, and Equations 7 and 11 give

$$W \geq \left(QC_B^0 + \frac{kQC_A^0}{(R_A - R_B)\lambda + k^*} \right) (t^* - R_B x/v) \cdot \exp(-\lambda R_B x/v) + \frac{kQC_A^0 (R_A - R_B)}{[(R_A - R_B)\lambda + k]^2} \left[\exp \frac{(-\lambda t^* - k(t^* - R_B x/v))}{R_A - R_B} - \exp(-\lambda R_B x/v) \right] \quad (12)$$

If $t^* > R_A x/v > R_B x/v$, then both C_A and C_B at the accessible environment are nonzero and Equations 7 and 11 give

$$\frac{W}{Q} \geq Q \left(C_B^0 + \Gamma \right) (t^* - R_B x/v) \exp(-\lambda R_B x/v) + \frac{Q\Gamma}{\alpha} \left\{ \exp - \left[\frac{(R_A \lambda + k^*)x}{v} \right] - \exp(-\lambda R_B x/v) \right\} + Q \left(C_A^0 - \Gamma \right) (t^* - R_A x/v) \exp \left[-\frac{(R_A \lambda + k^*)x}{v} \right] \quad (13)$$

where $\Gamma = \frac{k^* C_A^0}{(R_A - R_B)\lambda + k^*}$

$$\alpha = \frac{(R_A - R_B)\lambda + k^*}{R_A - R_B}$$

The detailed derivations of Equations 12 and 13 are given in Reference 20.

Step 4: Determination of Critical Parameter Combinations

Equations 12 and 13 were solved numerically for release limits and decay constants for ^{237}Np and ^{243}Am . Solutions are plotted as bivariate curves of $1/k^*$ and $1/R_B$ values with various combinations of values of the other parameters in Figures 4 to 7. The chemical-reaction parameter $1/k^*$ is analogous to the mean lifetime $1/\lambda$ of a radionuclide with respect to radioactive decay. It describes the stability of the relatively immobile species A to conversion to a more mobile species B.

Figure 4 shows solutions of Equations 12 and 13 for ^{237}Np for several values of x/v . Neptunium is assumed to be contained in the waste package for 1,000 years after waste emplacement and then is released from the engineered facility at a rate determined by a solubility-limited concentration C_A^0 of 10^{-7} moles/liter and a flux of water Q through the facility of 10^7 liters/yr. These parameters result in a neptunium source term QC_A^0 of 1.0 mole/yr.

Solutions to Equations 12 and 13 for ^{243}Am are shown in Figures 5-7. In these figures, the release limit for Am-243 was assumed to be 100 Ci/1000 MTHM. Release was assumed to start immediately after emplacement and the ground-water travel time to the accessible environment was 1000 years. The fractional release rate listed in the figure captions refers to the inventory at emplacement, 6.6×10^5 Ci (1.41×10^4 moles) for an assumed repository inventory of 46,800 MTHM of BWR and PWR spent fuel assemblies (cf. Reference 1).

Figures 5 and 6 demonstrate the effect of changes in R_A and C_0 (total concentration in the engineered facility), respectively, on the shapes of the curves when the initial concentration of a nonsorbing species B, C_B^0 , is very small but non-zero.

The sensitivity of the results to the near-field speciation of ^{243}Am is illustrated in Figure 7. In the three curves of this figure a small variation in the concentration of C_B^0 leads to profound changes in the shapes of the curves.

RESULTS

Application to EPA Standard and NRC Regulation

Retardation factors and reaction rates for the interconversion of the species of interest in HLW management generally are currently not available. The methodology developed in the previous sections, however, can be applied to available data as follows. If R_B equals 1.0, then species B is unretarded and migrates at the velocity of the ground water. For a given combination of release rate, ground-water travel time, and R_A , the value of k^* which corresponds to R_B equal to 1.0 can be obtained from Equation 13 and Figures 4-7 and is denoted k_m . This is the lower limit of the reaction rate constant that needs to be considered for performance assessment studies. In other words, if the reaction rate is lower than k_m , the conversion of A to B cannot cause a discharge of the radionuclide greater than its EPA release limit. This means that if a regulatory agency wished to use available sorption data to assure compliance of a site with the EPA standard, then it

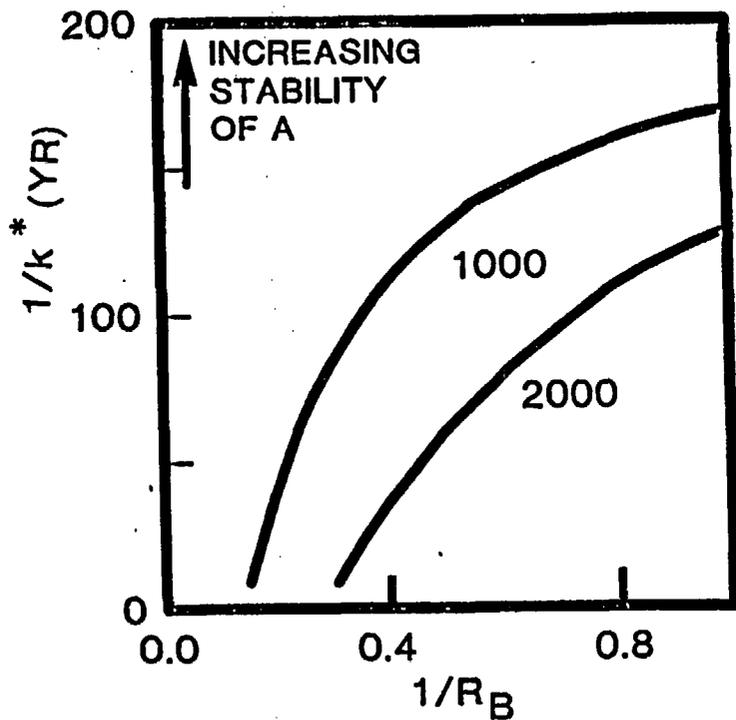


Figure 4. Combinations of Values of Reaction Rate Constant k^* and Retardation Factor R_B of Mobile Species B Which Lead to Discharge of ^{237}Np Equal to a Specified Release Limit. Curves for two values of ground-water travel time x/v are shown. Retardation factor $R_A = 200$; source term $QC_A^0 = 1.0$ mole/yr; containment period = 1,000 yr; Release limit = 20 curies (120 moles Np-237) per kiloton of heavy metal.

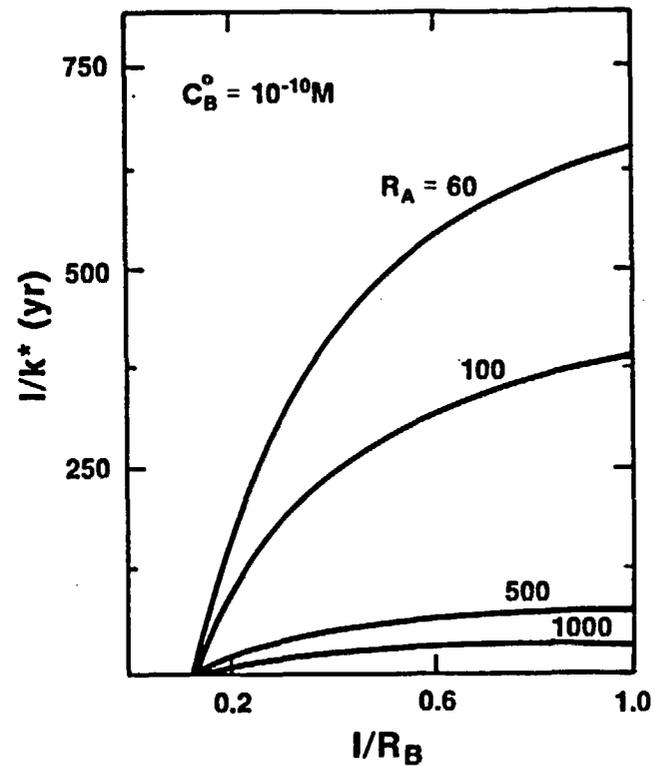


Figure 5. Effect of Retardation of Species A on EPA Compliance Curves (Annual Fractional Release Rate = 10^{-5} ; $Q = 1.4 \times 10^6$ liter/yr; $C_A^0 = 10^{-7}$ M; $t^* = 10,000$ yr; $t_0 = 0$ yr; $x/v = 1000$ yr; $C_B^0 = 10^{-10}$ M; $W_{\text{Am-243}} = 100$ Ci/1000 Metric Tons Heavy Metal, MTHM). Areas below curves correspond to violations of EPA standard. Each curve corresponds to a different value of the retardation factor for species A, R_A .

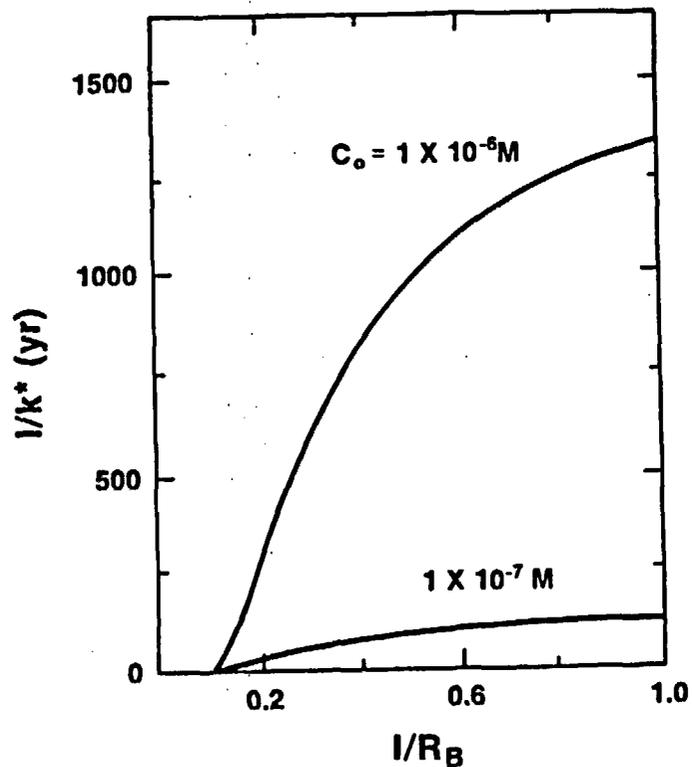


Figure 6. Effect of Near-Field Concentration of Am-243 (C_0) on EPA Compliance Curves ($R_A = 100$; $x/v = 1000$ yr; $t^* = 10,000$ yr; $W_{Am-243} = 100$ Ci/1000 MTHM; $t_0 = 0$ yr; $C_B^0 = 10^{-12}$ M; $Q = 1.4 \times 10^6$ liter/yr). Areas below curves correspond to violations of EPA standard. Note that $C_A^0 \approx C_0 =$ total concentration.

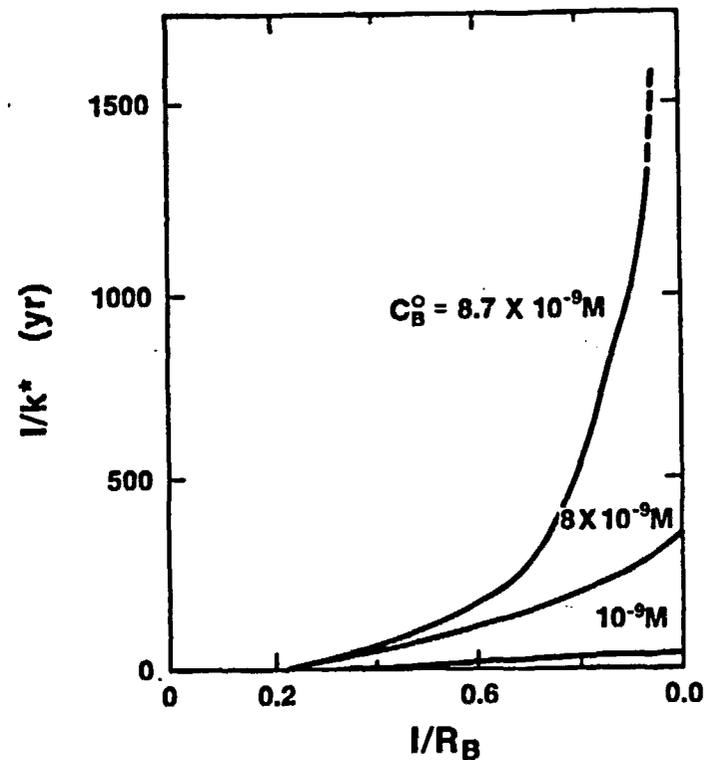


Figure 7. Effect of Near-Field Concentration of Species B on EPA Compliance Curves ($W_{Am-243} = 100$ Ci/1000 MTHM; $t^* = 10,000$ Yr; $C_0 = C_A^0 + C_B^0 = 3 \times 10^{-8}$ M; $Q = 1.4 \times 10^6$ liter/yr; $R_A = 300$; $x/v = 1000$ yr). Areas below curve correspond to violations of EPA standard for Am-243. Note that small changes in C_B^0 cause large changes in shapes of curves. For $C_B^0 = 8.7 \times 10^{-9}$ M, violation occurs due to initial inventory of species B alone for low values of R_B .

must be shown that the reaction rate constant is less than k_m . A conservative analysis (i.e., one that will overestimate radionuclide discharge) can be made by assuming that measured sorption ratios can be used to calculate values of R_A . The actual integrated discharge of a multi-species system of americium-243, for example, will be less than that of a two-species system in which R_D is zero and R_A is taken from the measured sorption ratios $R_{d,avg}$ for americium.

Table 1 lists R_A values for ^{237}Np and ^{243}Am for several geologic media calculated from available sorption and hydrogeologic data.1-3

Table 1
Retardation Factors Assumed for Species A of ^{237}Np and ^{243}Am

<u>Medium</u>	<u>^{237}Np</u>		<u>^{243}Am</u>	
	<u>Minimum</u>	<u>Mean</u>	<u>Minimum</u>	<u>Mean</u>
Basalt	35	1,500	60	1,600
Salt	10	500	110	2,400
Zeolitized Tuff	10	110	1,020	7,600
Vitric/ Devitrified Tuff	20	250	300	1,200

$R_A = 1 + \beta R_d$ where $\beta = \rho(1-\phi)/\phi$ for tuff and salt; $\beta = 2.3$ for basalt. Sources of data for density (ρ), porosity (ϕ) and sorption ratio R_d are References 1-3.

Extreme and mean values of density ρ and porosity ϕ were used to calculate the minimum and mean β values listed in the table. The ranges of R_A values presented in Table 1 represent conservative estimates of the actual ranges and uncertainty in available information on the sorptive properties of rocks from each of the geomedias listed. For each R_A value in the table, a minimum mean lifetime $1/k_m$ for species A, which would ensure compliance with an EPA release limit (20 or 100 Ci), was calculated. In this way, the uncertainty represented by ranges in R_A values was converted to ranges in values of $1/k_m$ for each rock type. The results of these calculations are presented in Figures 8 and 9 for ^{237}Np and ^{243}Am respectively. An annual fractional release limit of 10^{-5} per year, $R_B = 1$, and travel time of 1000 years were assumed; other parameter values are given in the figure captions.

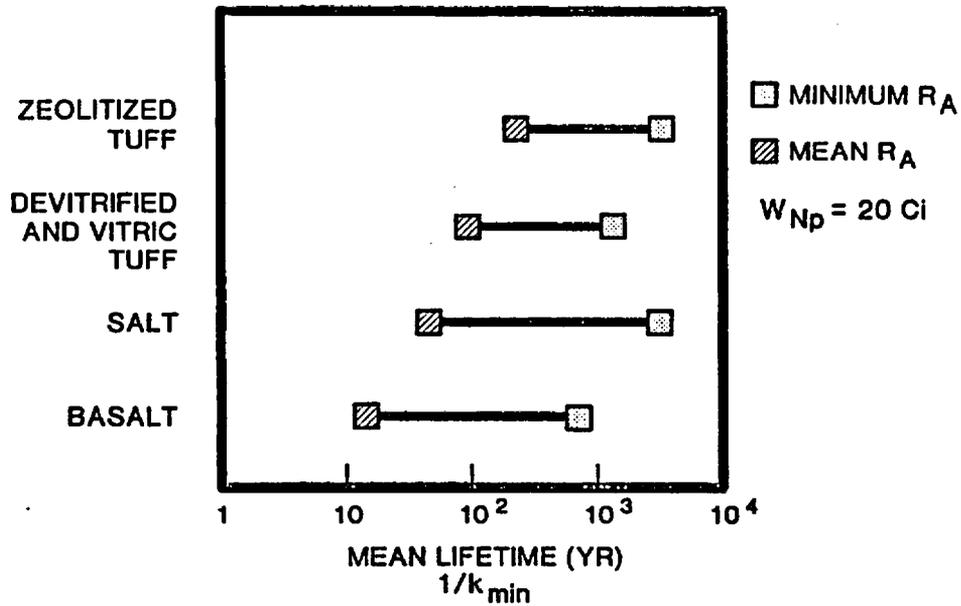


Figure 8. Media-Specific Chemical Stability of ^{237}Np Required to Comply With Release Limit of 20 Ci/1000 MTHM. ($t_0 = 1000$ yr, $QC_A^0 = 2.6$ moles/yr).

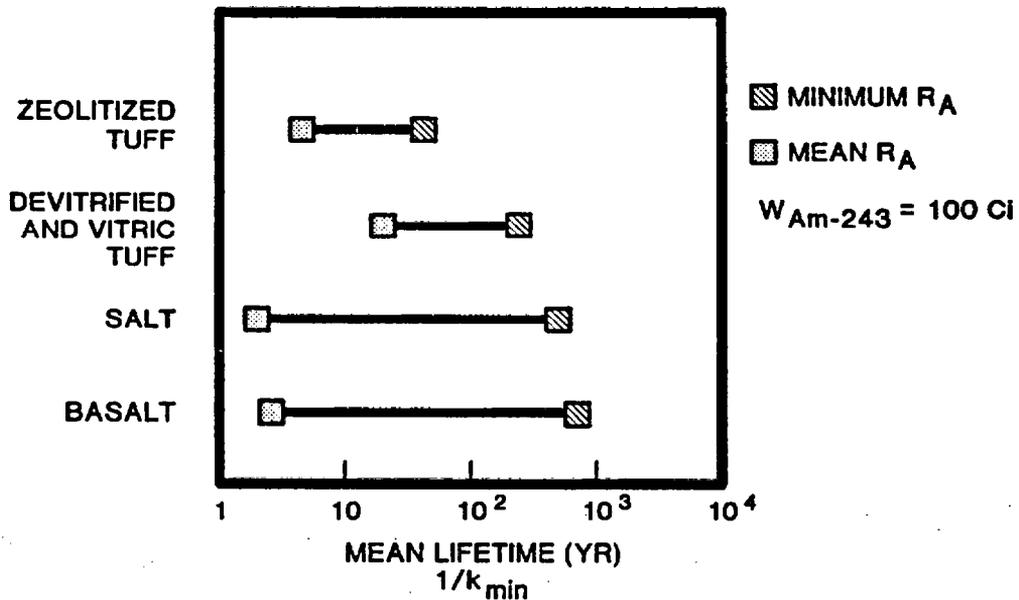


Figure 9. Media-Specific Chemical Stability of ^{243}Am Required to Comply With Release Limit of 1000 Ci/1000 MTHM. ($t_0 = 0$ yr, $C_B^0 = 1 \times 10^{-10}$ M, $Q(C_A^0 + C_B^0) = 0.14$ moles/yr).

Application to Experimental Design

In this section, the application of the calculated values of minimum chemical stability for neptunium-237 to the design of batch laboratory sorption experiments will be illustrated. It will be shown that it is possible to determine the required duration of kinetic and sorption experiments for quantitative observation of the effects of potential speciation reactions that could disguise violations of the EPA standard.

In a carefully designed batch experiment, it would be desirable to introduce the radioactive tracer in the same chemical form that is released by the waste (glass or spent fuel). The sorption ratio obtained from such an experiment may provide information about the sorption behavior of the species in the near-field environment. However, as discussed previously, it cannot be assumed that the chemical species released into the near field will remain stable indefinitely. Figures 2 and 10 depict hypothetical batch experiment and field scenarios in which species A, the initially dominant, more strongly sorbing species, converts irreversibly to species B, a more mobile species. Such a transformation could occur at a rate that is too low to detect in a batch sorption experiment yet still be significant on the time scale relevant to HLW disposal.

In a sorption experiment similar to that depicted in Figure 10, the material balances for species A can be represented as

$$dC_A/dt = -(m/v)dq_A/dt - kC_A \quad (15)$$

$$dq_A/dt = \rho h a (Rd C_A - q_A) \quad (16)$$

where m = mass of solid substrate

v = solution volume

q_A = concentration of A on solid

C_A = concentration of A in liquid

ρ = grain density

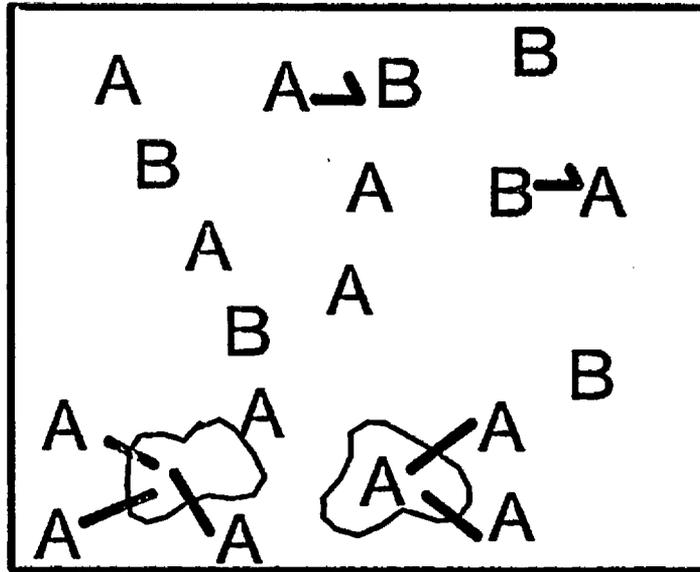
h = mass transfer coefficient for sorption

a = interfacial surface area per gram of solid

k = reaction rate constant.

The initial conditions are

$$C_A(t=0) = C_0 = \text{constant and } q_A(t=0) = 0 .$$



BATCH EXPERIMENT

Figure 10. Scenario for Geochemical Sensitivity Analysis. Conversion of hypothetical sorbing species A to a nonsorbing species B during a batch sorption experiment.

The term ρ_{ha} is the rate constant for the sorption reaction. If it is assumed that $Rd_B = 0$, then the material balances for species B can be written

$$\frac{dC_B}{dt} = kC_A \quad (17)$$

$$q_B(t) = 0 \quad (18)$$

with the initial condition of $C_B(t=0) = 0$ and all of the terms for species B are defined analogously to those for species A. Equations 15 to 17 were solved using Laplace transforms²⁰ to obtain

$$\frac{C_A + C_B}{C_0} = 1 + \frac{1}{(b^2 - 4C)^{1/2}} \left[(\rho_{ha} - b_1)(1 - k/b_1)e^{-b_1 t} - (\rho_{ha} - b_2)(1 - k/b_2)e^{-b_2 t} \right] \quad (19)$$

where
$$b_1 = \frac{-b + (b^2 - 4C)^{1/2}}{2}$$

$$b_2 = \frac{-b - (b^2 - 4C)^{1/2}}{2}$$

$$b = \rho h a \left(1 + \frac{m R d_A}{v} \right) + k$$

$$C = \rho h a k$$

Values of $(C_A + C_B)/C_0$ are shown in Figure 11 for values of k and $R d_A$ relevant to neptunium-237 and for values of the other parameters that may be typical for batch sorption experiments.^{20,21} The curve shows that if species A converts irreversibly to species B, then the concentration of neptunium in solution will initially decrease rapidly as species A is sorbed by the solid, reach an apparent steady state for several days, but then increase as significant amounts of species A convert to the poorly sorbed species B. Figure 12 shows that the time needed for the solution concentration to rise detectably above the "steady state" concentration depends on the experimental precision of the analytical techniques used to monitor the solution concentration, as well as the values of $1/k$ and R_A . If the precision were equal to ϵ_1 , then after t_1 days it would be clear that the solution concentration had not reached steady state and that speciation reactions unaccounted for by a simple sorption model were occurring.

Discussion

Use of the methodology for geochemical sensitivity analysis as developed in this paper can be illustrated as follows. A range of retardation factors for a radionuclide (eg. ²³⁷Np) can be obtained from data from laboratory and/or field studies for a potential HLW repository site. Equations 12 and 13 can be used to calculate a corresponding range of chemical stabilities which ensure that discharges of the radionuclide will not exceed a given limit (see for example Figure 7). Pairs of values of R_A and k_m obtained in this way could be used in Equation 19 to produce graphs such as Figure 11. From these graphs and from knowledge of the analytical precision of the method used to monitor solution concentration in the batch test, it is possible to determine the duration of the experiment required to quantitatively observe speciation effects that could lead to unforeseen violations of the EPA standard (or any other specified release limit). Thus, from Equations 12 and 13, if it is assumed that the retardation factor calculated for neptunium from batch sorption experiments is not lower than 1000; the groundwater travel time at the site is at least 1000 years; the waste isolation period is at least 1000 years; the annual fractional release rate of neptunium is 10^{-5} or less, and only one aqueous Np species is present in the near field, then $1/k_m$ must be at least 1.5 years. Figure 11 shows that batch experiments for neptunium should run at least t_2 days before it can be concluded that no potential speciation effects can cause unforeseen violations of the EPA standard if the analytical precision is ϵ_2 . In other words, if the above assumptions

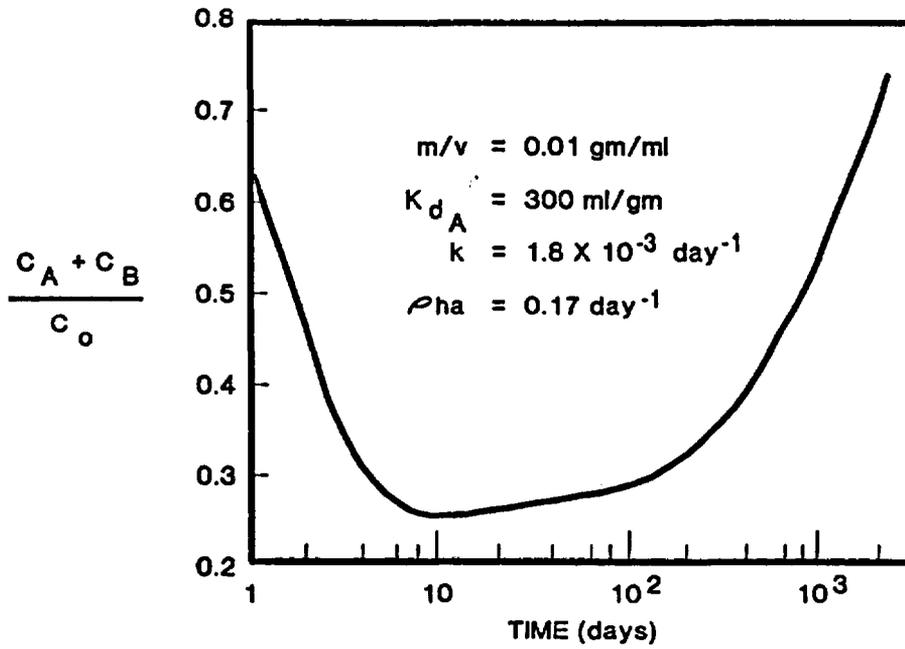


Figure 11. Relative Concentration in Batch Experiment Solution Calculated From Equation 19 for Scenario in Which Sorbing Species Converts Irreversibly to Nonsorbing Species. See text for definition of variables.

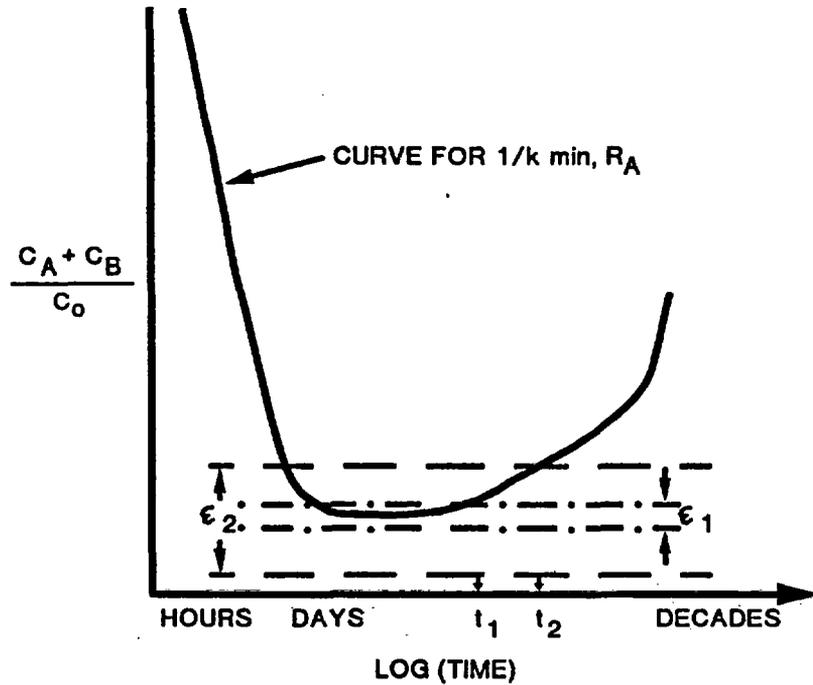


Figure 12. Relationship Between Analytical Precision ϵ_1 and Experimental Run Time t_1 Required to Observe Disequilibrium Due to Irreversible Conversion of A B.

about the site and waste package are valid, then even if the detailed speciation of neptunium along far-field migration paths is not known, sorption data from a batch experiment can be used to obtain bounding estimates of potential radionuclide discharges with confidence. Even if the actual discharge is not known (or knowable) it would be possible to know whether or not the discharge will exceed the EPA release limit.

Figures 7, 8, and 10 are based on an assumed R_B value of unity. This is the most conservative value of R_B that is possible and this value leads to conservative estimates of $1/k$ and design criteria for batch sorption experiments. In some cases the minimum required chemical stability consistent with $R_B = 1.0$ may not be demonstrable with available technology. The use of R_B values estimated from geological and thermochemical data for radionuclide species would produce a more realistic estimate of $1/k$ and more achievable experimental design specifications. Estimates of $1/k$ combined with estimates of R_B would enable the NRC and DOE to identify radionuclides for which the available sorption data are sufficient to carry out performance assessment calculations. The results of such an analysis could also be used to determine when complex phenomenological models (coupled reaction-flow models) are truly required for repository performance assessment.

Conclusion

Potential aqueous speciation reactions introduce uncertainty into performance assessment calculations designed to assess the compliance of nuclear waste repositories with the proposed EPA Standard (40CFR Part 191). In this report, a method was illustrated for determining hydrologic and geochemical conditions where such reactions could significantly affect the integrated radionuclide discharge. A minimum chemical stability can be described for radionuclide species examined in laboratory studies in order to assure compliance with the EPA Standard. The above method can be used by regulatory agencies to prioritize research needs and to evaluate published or ongoing radionuclide transport studies. The calculations may be used to determine the criteria for experiments designed to quantitatively observe the effect of important chemical speciation reactions.

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APPROXIMATE METHODS TO CALCULATE RADIONUCLIDE DISCHARGES FOR PERFORMANCE ASSESSMENT OF HLW REPOSITORIES IN FRACTURED ROCK K. L. Erickson, M. S. Y. Chu, M. D. Siegel, Sandia National Laboratories, Albuquerque, NM 87185.*

Performance assessment requires calculating radionuclide discharges for many sets of conditions for several scenarios. General application of rigorous convection-diffusion radionuclide transport models is impractical for repositories in fractured, porous rock. While such rigorous calculations are desirable for demonstrating detailed understanding of physicochemical phenomena, those calculations are often unnecessary for risk assessment if an upper bound for radionuclide discharges can be obtained from more approximate models. To minimize the number of rigorous computations required for performance assessment, three approximate methods for calculating radionuclide discharges in fractured, porous rock were evaluated: (1) a porous medium approximation where radionuclide diffusion rates into the matrix are proportional to depletion rates in the fracture fluids; (2) a linear-driving-force approximation where radionuclide diffusion rates into the matrix are proportional to the difference between bulk concentrations in the matrix and the fracture fluids, and (3) a semi-infinite-medium approximation where radionuclide diffusion rates into the matrix are calculated assuming a semi-infinite matrix. In this paper, the above three methods will be described; criteria for application of each given, and the respective uncertainties in calculated cumulative radionuclide discharges assessed. Furthermore, the applicability of each method to performance assessment for repositories in basalt, granite, and tuff will be shown using site-specific hydrologic and geochemical parameters.

The criteria for application of each method were derived from a general consideration of fluid residence times in the fractures and relaxation times for radionuclide concentration gradients in the matrix. The same criteria were then obtained from the solution to the transport equations for specific cases involving radioactive decay, chemical reaction, and varying matrix properties. For example, if fluid flow in saturated rock is one-dimensional and primarily occurs in parallel fractures having relatively uniform aperture $2b$ and spacing $2B$, and if matrix porosity ϕ_m , grain density ρ_g , fracture porosity ϕ_f , and sorption isotherms $f(C)$ in the matrix are relatively uniform, then the porous medium approximation applies when

$$x/v > 50 B^2 \alpha^2 \phi_f / \phi_m D (1 - \phi_f) \quad ;$$

the linear-driving force applies when

$$x/v > 0.2 B^2 \alpha^2 \phi_f / \phi_m D (1 - \phi_f) \quad ,$$

and the semi-infinite medium applies when

$$x/v < B^2 \alpha^2 \phi_f / \phi_m D (1 - \phi_f) \quad .$$

Here, D is the radionuclide diffusion coefficient in the pore water; v is the average fluid velocity in the fractures; x is the radionuclide transport path length, and α is a tortuosity/constrictivity factor for the matrix.

Site specific data for tuff¹ and granite² were used with the above criteria. Results indicate that for tuff, the porous medium approximation usually should be valid even for relatively thin beds ($x = 30m$), and that the linear-driving force or semi-infinite medium approaches are necessary only for extreme cases. For granite, the semi-infinite medium or linear-driving-force approaches may be required, while the porous medium approximation may be applicable only to relatively large granitic bodies.

The uncertainties in calculated discharge are assessed by comparing breakthrough curves calculated using the three approximations and exact solutions for a system of parallel fractures.

For comparison, discharges for conditions satisfying the criteria for the linear driving force and porous medium approximations are also calculated with the Network Flow and Transport Model/Distributed Velocity Method (NWFT/DVM) computer code. NWFT/DVM, a finite-difference code, was developed at Sandia National Laboratories for use in performance assessment calculations of HLW repositories. This code simulates the transport of radionuclides by ground water in both fractured and porous rock. Diffusion into the matrix is assumed to be driven by a concentration gradient that is linear from the fracture into the matrix. Alternatively, radionuclide transport can be simulated using an equivalent porous medium approximation with an appropriate retardation factor³.

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 August 1985

THIS IS AN ESTIMATE ONLY AND MAY NOT MATCH THE INVOICES SENT TO NRC BY SANDIA'S ACCOUNTING DEPARTMENT.

	Current Month	Year-to-Date
I. Direct Manpower (man-months of charged effort)	1.2	14.3
II. Direct Loaded Labor Costs	12.0	139.0
Materials and Services	0.0	0.0
ADP Support (computer)	0.0	2.0
Subcontracts	39.0*	159.0*
Travel	0.0	6.0
Other	1.0	0.0
TOTAL COSTS	52.0*	310.0*

Other = rounding approximation by computer

III. Funding Status

Prior FY Carryover	FY85 Projected Funding Level	FY85 Funds Received to Date	FY85 Funding Balance Needed
67.6K	302.60K	235K	None

* August expenditures for subcontracts do not reflect actual costs and will be adjusted in September progress report.