TABLE 4

Solubilities of Radioelements in Reference Basalt Ground Water (Column 2, Table 1) at 25°C Calculated at Sandia Labs (SNLA) and at Rockwell Hanford Operations (RHO)

	SNLA			RHO		
ELEMENT	SOLUBILITY (Log Molality)	STABLE SOLID	DOMINANT AQUEOUS SPECIES	SOLUBILITY (Log Molality)	STABLE SOLID	DOMINANT AQUEOUS SPECIES
Se	<-16.0 -12.6	Se	SeO_3^{-2}	-7.3	Se	**HSe^-
Zr	-6.0 (-5.6)	$ZrSiO_4$	$Zr(OH)_5^-$	-8.7	$ZrSiO_4$	$Zr(OH)_5^-$
Tc	<-16.0 (<-16.0)	TcO_2	TcO_4^-	-14	NG	NG
Pd	-5.4 (-5.4)	$Pd(OH)_2$	$Pd(OH)_2^o$	-9.8	**Pd	$Pd(OH)_2^o$
Sn	-14.1 (-14.8)	SnO_2	*$SnO(OH)F^o$	-17.7	SnO_2	$SnO(OH)^+$
Sb	>-2.0 (>-3.5)	Sb_2O_4	$HSbO_2^o$,$Sb(OH)_3^o$	-6.8	**$Sb(OH)_3$	$HSbO_2^o$,$Sb(OH)_3^o$
I	>-1.0	none	I^-	NG	NG	NG
Cs	>-1.0	none	Cs^+	NG	NG	NG
Sm	-7.9 (-8.0)	$Sm_2(CO_3)_3$	*$SmCl^+$	-9.1	**$Sm(OH)_3$	**$Sm(OH)_3^o$,**$Sm(OH)_4^-$ **$SmCO_3^+$

TABLE 4 (continued)

ELEMENT	SNLA SOLUBILITY (Log Molality)	SNLA STABLE SOLID	SNLA DOMINANT AQUEOUS SPECIES	RHO SOLUBILITY (Log Molality)	RHO STABLE SOLID	RHO DOMINANT AQUEOUS SPECIES
Pb	-4.9 (-4.5)	$PbCO_3$	$PbOH^+$, $Pb(OH)_2^o$ $PbCO_3^o$	-7.6	**$Pb(OH)_2$	$PbCO_3^o$, $Pb(CO_3)_2^{-2}$
Ra	-7.2 (-6.7)	$RaSO_4$	Ra^{+2}	-8	NG	NG
Th	-14.1 (-14.7)	ThO_2	$Th(OH)_4^o$	-14.1	ThO_2	$Th(OH)_4^o$
Pa	(>-1.0)	PaO_2	$Pa(OH)_2^+$	NG	NG	NG
U	-15.9 (-15.3)	UO_2(cr)	$U(OH)_5^-$	-9.7	**$USiO_4$	$U(OH)_5^-$
Np	-8.9 (-9.7)	NpO_2	$NpO_2HCO_3^o$	-10.0	NpO_2	$Np(OH)_5^-$
Pu	<-16.0 (<-16.0)	PuO_2	$Pu(OH)_4^o$	-9.4	PuO_2	**$PuCO_3^{2+}$
Am	> -1.0 (>-1.0)	AmO_2	$AmOH^{+2}$	-7.9	**$Am(OH)_3$	**$Am(CO_3)_2^-$, **$Am(CO_3)_3^{-3}$, **$AmCO_3^+$

* Species or solid not included in RHO data base

** Species or solid not included in SNLA data base

( ) solubility calculated at 55°C

NG-not given

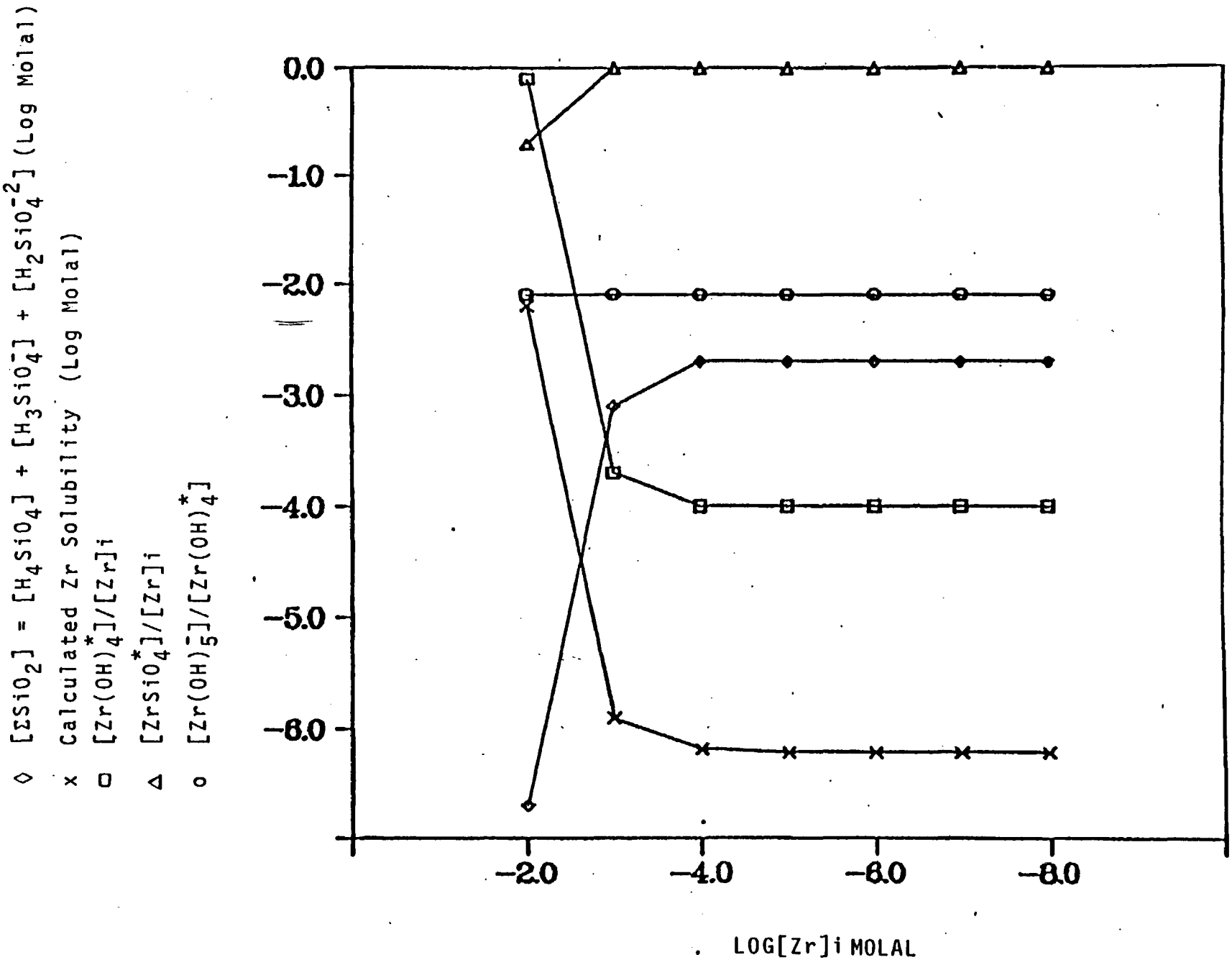

Figure 1 Relationship between calculated Zr solubility, silica, Zr solid phases and total Zr concentration

Attach 1-2

LETTER REPORT

CALCULATIONS OF SENSITIVITY OF RADIONUCLIDE DISCHARGE TO RATE CONSTANTS FOR REACTIONS BETWEEN RADIONUCLIDE SPECIES

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A. Introduction

Simple algorithms using sorption ratios (Rd)* are used to calculate radionuclide retardation factors in the transport codes currently employed in performance assessment (Cranwell, et al., 1982). Sizeable uncertainties exist in the values of geochemical and hydrogeological parameters used to characterize possible contaminant flow-paths. Large numbers of calculations** using combinations of the input variables are used to translate the uncertainty in the site characterization data into probabilistic risk analysis. The costs of performing large numbers of calculations favor the use of retardation factors in performance assessment studies.

The sorption ratio (Rd) is a well-established, albeit controversial method of empirically characterizing the interaction between rocks and radionuclides in solution. Early measurements were plagued by unacceptable variability and irreproducibility. Recent improvements in experimental techniques, however, have led to reasonable agreement between different laboratories and methods (Serne and Relyea, 1982; Wolfsberg, et al., 1981; Guzowski, et al., 1983). Although a standardized method for measuring Rd's has not been established, current techniques commonly include: determination of sorption isotherms, preequilibration of site-specific groundwater and rocks and precautions to avoid supersaturation of the reaction solution with the radionuclide. A large number of Rd values have been published for a variety of rock types and pure materials.

These improvements in laboratory techniques however, have done little to solve an important weakness of the sorption ratio approach, particularly when the ratios are obtained by

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*We use the symbol Rd to signify an experimentally-determined radionuclide distribution coefficient where we do not assume that equilibrium has been achieved. Although they are called "sorption ratios," there is no assurance that sorption is the only chemical process occurring during the experiments. We use the term Kd to denote ideal linear ion exchange equilibrium involving trace constituents.

**In a study of a Hanford basalt repository site, Hunter (1983) has identified more than 100 radioactive waste release scenarios with non-trivial probabilities. The analysis of a single scenario may involve more than 100 transport calculations. Preliminary ground-water flow modeling may show that some of these scenarios need not be considered in subsequent transport modeling efforts; however, it is clear that a probabilistic risk assessment for a single site will require thousands of calculations.

batch methods. Available Rd data do not account for the existence of multiple aqueous species.

Sorption ratios obtained by batch methods describe the "average" or bulk sorption behavior of all species of the radionuclide present in the reaction solution. When several aqueous complexes of the nuclide are present, it is likely that at least one will migrate at a rate faster than predicted by the "average" Rd value (Coles and Ramspott, 1982; Serne and Relyea, 1982). In addition, in batch experiments, radionuclides are generally not introduced into the reaction solution as the species that would be released from the waste form in a repository. The degradation of borosilicate glass, for example, may release neutral or anionic aqueous radionuclide complexes or pseudocolloids containing radionuclides (Salter, et al., 1981a,b; McVay and Buckwalter, 1982). Such species may migrate at rates that approach that of the groundwater (Champ, et al., 1982; Coles and Ramspott, 1982). The rate at which these complexes convert to species that are stable in the laboratory reaction solutions or in the repository far field has not been considered in previous studies. These deficiencies in the batch method and previous transport calculations introduce a measure of uncertainty in performance assessment calculations. It is important, therefore, to identify those radionuclides for which the use of a bulk Rd value alone will cause gross underestimations of integrated radionuclide discharges and disguise possible violations of the EPA Standard.

This paper has two major objectives. The first is to describe in general terms hypothetical scenarios involving types of reactions between aqueous complexes of radionuclides and groundwater ligands that will affect radionuclide discharge at the accessible environment. The second objective is to demonstrate a method for assessing the sensitivity of radionuclide discharge to the occurrence of a particular type of reaction. The mathematical development presented is specific to one particular process; however, the general approach and method will be applicable to a variety of chemical behaviors.

B. Existence of Multiple Radionuclide Species

An element can exist in solution in a large variety of aqueous complexes. For example, Early, et al. (1982), list 47 different potential species for uranium in natural waters, and Duda , et al. (1982), list 13 different aqueous species for iodine. In general only one or two aqueous species will be important under a particular set of physico-chemical conditions. Changes in speciation (i.e., transformation from one set of dominant species to another) may occur in response to variations in Eh, pH, temperature, or concentrations of the element, complexing ligands or competing cations. It is

possible that such alterations to the groundwater may occur in the rock volume surrounding a repository during the 10,000-year period following the emplacement of nuclear waste. Changes in the thermal field of the repository as the waste decays, mixing of different groundwaters in the far field, and interactions between the groundwater, wall rock, and waste package may alter the initial chemical composition of the water and the speciation of the radionuclides.

There are numerous types of chemical reactions that can affect radionuclide speciation. The reactions can be reversible or irreversible. The kinetics of the reactions may be first order (i.e., involving interactions of one radioelement molecule or ion at a time), or higher order (involving interactions of several complexes at once). Strongly sorbing species can be converted to nonsorbing species or vice versa. Table 1 gives examples of different types of reactions. Note that any reaction can be described by all of the categories listed in the table. For example, a reaction can be reversible, first order, and involve conversion of a species that is strongly retarded to a complex that is nonsorbing.

C. Radioactive Decay and Production

The EPA Draft Standard (40 CFR 191) sets limits for the releases of individual radioisotopes and not total elemental releases. During the 10,000-year period regulated by the EPA Draft Standard, the relative amounts of radioelements in the waste form, groundwater, and wall rock will change due to radioactive decay and production. All isotopes of an element behave in approximately the same manner in a given chemical reaction; however, the total amount of the element in the system will vary due to radioactive decay and/or production. This variation is a function of both the initial inventory (i.e., actual amounts long-lived and short-lived isotopes and parents) as well as the half-lives of the isotopes (see Table 2). The chemical behavior of an element (i.e., solubility, speciation, sorption, and transport, etc.), however, is determined by the total amount of all isotopes of the element. Thus, the release rate of any radionuclide of a given element will be influenced by the production, decay, and transport of other isotopes of that element.

The radioisotope inventory for the reference repositories in basalt and tuff environments in previous Sandia studies is shown in Table 2 (Pepping, et al., 1983; Siegel and Chu, 1983). Based on the inventory and toxicity of each radionuclide, the following chains of radionuclides are considered in the SNLA performance assessment methodology:

1. $^{240}Pu \rightarrow {}^{236}U \rightarrow {}^{232}Th \rightarrow {}^{228}Ra$

2. $^{245}Cm \rightarrow {}^{241}Pu \rightarrow {}^{241}Am \rightarrow {}^{237}Np \rightarrow {}^{233}U \rightarrow {}^{229}Th$

3. $^{246}Cm \rightarrow {}^{242}Pu \rightarrow {}^{238}U \rightarrow {}^{234}U \rightarrow {}^{230}Th \rightarrow {}^{226}Ra \rightarrow {}^{210}Pb$

   $^{238}Pu \rightarrow {}^{234}U$

4. $^{243}Am \rightarrow {}^{239}Pu \rightarrow {}^{235}U \rightarrow {}^{231}Pa \rightarrow {}^{227}Ac$

The fission and activation product radionuclides ^{99}Tc, ^{129}I, ^{126}Sn, ^{90}Sr, ^{14}C, ^{135}Cs, and ^{137}Cs are also considered in the methodology.

In some cases, a single isotope may account for nearly all of the concentration of a radioelement in the system. For example, the inventory of the reference spent fuel repository assumed in NUREG-3235 (Pepping et al., 1983; Siegel and Chu, 1983) contained 3,500 curies (2,420 moles) of ^{234}U and 15,000 curies (1.89×10^8 moles) of ^{238}U (Table 2). Clearly, the change in uranium concentration in the waste form or groundwater due to decay of ^{234}U will be minor. Production of uranium by decay of its radiogenic parents, ^{240}Pu, ^{242}Pu, ^{237}Np and ^{239}Pu during the 10,000-year EPA regulatory period will be less than 2×10^6 moles. To a first approximation, then, the decay and production of uranium by radioactive processes can be ignored in many far-field speciation calculations.*

If the waste package isolates the radionuclides for 500 to 1,000 years following closure of the repository, several isotopes will decay to very low levels. The contribution of these radioisotopes to total elemental concentrations may be ignored in far-field transport and speciation calculations. For example, the large amount of ^{137}Cs that is present in the initial inventory of spent fuel (Table 2) decays to very low levels during a 300 year isolation period due to its short half-life

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*There are many calculations in which radioactive decay and production cannot be ignored. Calculations involving the EPA Draft Standard, as discussed above, deal with the release limits of individual isotopes. Studies of rates of release of radioelements from the waste package into the near field may require consideration of individual isotopes. The release rate of a radionuclide may depend upon the leach rate of its radiogenic parent. Although an element may be released slowly directly from the waste form, its isotopes could have radiogenic parents which have high leach rates. The concentration of the element in the near field would then depend on the leach rates, concentrations and half-lives of the parent radioisotopes.

(30 yr.). This means that the long-term behavior of Cs from the waste will be controlled by ^{135}Cs ($t_{1/2}$ = 2.0E6 yr.) even though this isotope is less abundant than ^{137}Cs in the initial inventory.

The radionuclides can be subdivided into different groups based on whether or not decay or production is significant during the isolation period mandated by the N.R.C. regulation 10 CFR 60 or during the 10,000-year EPA regulatory period. Table 4 shows such a classification for several radionuclides.

Consideration of initial inventories and half-lives of radionuclides as discussed above can lead to a number of simplifying assumptions in speciation and transport calculations for different radioelements in different scenarios. This point will be illustrated further in Section D.2 of this report.

D. General Mathematical Development and Application

In Part 1 of this section, it will be shown how effects of chemical speciation reactions can be included into a transport equation. The application of this equation to assessments of compliance with the EPA Draft Standard will be discussed in general terms. In Part 2 of this section, the methodology will be applied to discharge of ^{237}Np. Development of the equations used in this example is discussed in the Appendix.

1. Basic Equations

If radionuclide i is initially present in the inventory but is not subsequently produced as a daughter product, a basic transport equation for nuclide i can be written as*

$$\frac{\partial C_i}{\partial t} = -v\frac{\partial C_i}{\partial x} - \frac{1}{m}\frac{\partial q_i}{\partial t} - \lambda C_i - \frac{\lambda}{m} q_i - \sum Z_i \qquad (1)$$

where

C_i = concentration of i in solution (mole/cc),
m = void ratio = $\phi/(1-\phi)\rho$,
ϕ = effective porosity,
λ = decay constant for radionuclide i,
q_i = concentration of i in solid (mole/gm),
v = interstitial fluid velocity,
x = direction of fluid flow,
ΣZ_i = other reactions involving radionuclide i,
ρ = grain density of the matrix rock, gm/cm^3.

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*Justification for omitting the dispersion term is given later.

If there is a single species of radionuclide i in the system, if the system is a porous media and if sorption is reversible and linear over the concentration ranges that exist in the system,* then we can define the retardation factor for radionuclide i as

$$R_i = 1 + Kd_i \, \rho \frac{(1-\phi)}{\phi} = 1 + q_i/C_i m \qquad (2)$$

where

Kd_i = equilibrium radionuclide sorption distribution coefficient, cm^3/gm .

It is possible to define the reaction terms Z_i of Equation (1) to include the effects of chemical speciation on the discharge of radionuclide i. Consider a reaction in which one chemical species A_i of radionuclide i is converted to another chemical species B_i by reaction with groundwater ligands:

$$nA_i + mL \underset{k_i^r}{\overset{k_i^f}{\rightleftharpoons}} B_i$$

where k_i^f and k_i^r are the rate constants of the forward and reverse reactions, respectively, and the ligand L is in approximately constant concentration in the system. Let r_A represent the rate of depletion of A, and r_B represent the rate of production of B. Then assume that the reaction is first order, i.e.,

$$r_A = k_i^f C_A C_L = kC_A = r_B \quad .$$

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*The assumption of linear sorption in the far field of the repository is not unreasonable. Dilution and dispersion of the radionuclides by ground-water flow in the 2 km controlled zone of the repository will probably produce low radionuclide concentrations. This important assumption will be tested in Subtask 8A in the proposed work "Geochemical Sensitivity Analysis." If it is determined that sorption can be nonlinear over expected ranges of radionuclide concentration, then the concentration dependence of the sorption equilibrium distribution coefficient will be included in the equations in Section D and in the Appendix.

If nuclide i is initially present in the inventory but is not subsequently produced as a daughter product, then we can write a separate transport equation for each chemical species as

$$\frac{\partial C_A}{\partial t} + v\frac{\partial C_A}{\partial x} = -\frac{1}{m}\frac{\partial q_A}{\partial t} - kC_A - \lambda C_A - \frac{\lambda}{m}q_A \qquad (3)$$

$$\frac{\partial C_B}{\partial t} + v\frac{\partial C_B}{\partial x} = -\frac{1}{m}\frac{\partial q_B}{\partial t} + kC_A - \lambda C_B - \frac{\lambda}{m}q_B \qquad (3')$$

where

C_A = concentration of A in solution (mole/cc)
C_B = concentration of B in solution (mole/cc)
q_A = concentration of A in solid (mole/gm)
q_B = concentration of B in solid (mole/gm)

and m, λ, v, and x were defined previously.

If we define:

R_A = retardation factor for A

$$R_A = 1 + Kd_A\frac{\rho(1-\phi)}{\phi} = 1 + \frac{q_A}{C_A m}$$

R_B = retardation factor for B

$$R_B = 1 + Kd_B\frac{\rho(1-\phi)}{\phi} = 1 + \frac{q_B}{C_A m}$$

where

Kd_A = sorption equilibrium distribution coefficient for A (cc/gm)
Kd_B = sorption equilibrium distribution coefficient for B (cc/gm)
ρ = grain density

then Equations (3) and (3') can be rewritten as:

$$\frac{\partial C_A}{\partial t} + \frac{v}{R_A}\frac{\partial C_A}{\partial x} = -\frac{(k + \lambda R_A)C_A}{R_A} \quad . \qquad (4)$$

$$\frac{\partial C_B}{\partial t} + \frac{v}{R_B}\frac{\partial C_B}{\partial x} = \frac{kC_A}{R_B} - \lambda C_B \quad . \tag{4'}$$

Solution of these equations gives C_A and C_B at any time or position along the flow path as a function of v, k, λ, R_A, and R_B. The solutions for a step-function source term are given in the Appendix and correspond to a controlled release over a given time period.*

Those solutions can be used in the following manner: Consider the case where $R_A >> R_B$, i.e., species A is an immobile species and B is a mobile complex. Assume that radionuclide i has a half-life much greater than 10,000 years, that the reaction $A + L \rightarrow B$ is irreversible.** Integration of C_B with respect to time and volumetric flux provides the integrated radionuclide discharge associated with species B over the regulatory period

$$Q \int_{t=0}^{t=10,000} C_B dt = f(x, v, R_A, R_B, k, Q) \tag{5}$$

where Q = fluid discharge (cm^3/yr).

Assume that the value of R_A is large enough to preclude violations of the EPA Standard due to release of A alone. For a given scenario, we can determine v, Q, and x and set the discharges of species A and B equal to the EPA Release Limit for nuclide i.

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*The reason for omitting the dispersion term in Equation (2) was as follows: for a given time t, dispersion would tend to spatially spread the concentrations C_A and C_B, but the cumulative discharge of C_A and C_B would be relatively unaffected except possibly at some values of t near $R_B x/v$ or $R_A x/v$.

**This case is one of many possible reactions involving A, B, and groundwater ligands L. The irreversible conversion of an immobile species A to a mobile species B without dispersion is a "worst case" scenario. The discharge of radionuclide i would be less if the reaction between A and B were reversible and/or if radionuclide i decays appreciably during the 10,000-year period.

$$Q \int_{t=0}^{t=10,000} (C_A+C_B)dt = g(R_A,R_B,k) = W_i \qquad (6)$$

where W_i = EPA Release Limit for nuclide i. We can then determine combinations of R_B and k which lead to compliance or violations of the EPA Standard for given values of R_A.

When Equations (4) and (4') are solved and integrated in the manner described in the Appendix, the following expression is obtained:

$$W_i \geq QA_i^o \left[t^* - R_B x/v + \frac{R_A - R_B}{k} \left[\exp\left(\frac{-k(t^* - R_B x/v)}{R_A - R_B} \right) - 1 \right] \right]$$

$$+ QA_i^o \exp(-kx/v) \left[\frac{(R_A - R_B)}{k} \right] \left[1 - \exp\left(\frac{-k(t^* - R_A x/v)}{R_A - R_B} \right) \right] \qquad (7)$$

where A_i^o is the concentration of species A at the repository, t^* is the period of release, and the other terms have been defined above.

2. Application

Equation (7) can be applied to the discharge of neptunium under certain conditions. The radioactive decay and production of the ^{237}Np, the single isotope of Np in waste can be represented as

$$^{245}Cm \rightarrow {}^{241}Pu \rightarrow {}^{241}Am \rightarrow {}^{237}Np \rightarrow {}^{233}U \quad .$$

Examination of the half-lives and inventories of the above radionuclides (cf. Tables 2, 3) show that radioactive production of neptunium will be largely complete within 1,000 years after the emplacement of the waste. The long half-life of ^{237}Np ensures that decay of Np will be insignificant during the 10,000-year EPA regulatory period.

Figure 1 shows solutions of Equation (7) for Np-237 for time $t^* \geq R_A x/v > R_B x/v$. The assumed repository dimensions are given in Pepping, et al., 1983, and Siegel and Chu, 1983. 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 A_i 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 (QA_i^o) of 1.0 mole/yr.

Several features of Figure 1 deserve discussion. The axes 1/k and $1/R_B$ were chosen primarily to allow a clear separation of the areas on the graphs which correspond to violations of the EPA release limit from the areas corresponding to compliance with the limit. Discharge of ^{237}Np for points on the curves is equal to the EPA release limit for neptunium. Points lying below the curves correspond to violations of the EPA Standard by this radionuclide. The parameter 1/k is analogous to the mean lifetime $1/\lambda$ of a radionuclide in radioactive decay. It describes the stability of the relatively immobile complex A with respect to conversion to a more mobile complex B. From these curves, it is possible to obtain critical combinations of values of R_A, R_B and k such that discharge of ^{237}Np will exceed the EPA release limit (120 moles/1,000 MTHM) under the specified conditions.

The sensitivity of the critical parameter combinations to variations in the source term QA_i^o and groundwater travel time x/v is illustrated on Figure 2 and Figure 3, respectively. The curves in the three diagrams have the same general shape:
1. an asymptotic approach of $1/R_B$ to the assumed value of $1/R_A$ as 1/k approaches zero and 2. a flattening of the slope of the curves as $1/R_B$ approaches 1.0. The former of these two characteristics can be understood as follows: as R_B approaches R_A, the migration veolocity of species B approaches that of species A. The rate of conversion of A to B (k) must increase to maintain a constant discharge along the curve. When $R_A = R_B$, there is no difference between species A and B in these calculations and the rate of conversion $A \rightarrow B$ is effectively infinite (i.e. $k \rightarrow \infty$; $1/k \rightarrow 0$).

The flattening of the curves as $1/R_B \rightarrow 1.0$ is a consequence of the exponential nature of the relationship of equation (7) and the choice of $1/R_B$ as an axis, (i.e. a reciprocal of a parameter). If $R_B = 1.0$, then species B is unretarded and migrates at the velocity of the ground water. The corresponding value of k is the lower limit of the reaction rate that need be considered for the conditions specified in the figure caption. In other words, if k is lower than this value, the conversion of $A \rightarrow B$ cannot cause a discharge of ^{237}Np greater than the EPA release limit no matter what the value of R_B. In the next section, it will be shown that identification of these critical parameter values by the N.R.C. can help to prioritize research needs and evaluate field and column radionuclide migration experiments where speciation effects must be considered.

3. Discussion

Calculations similar to those outlined in section D.2,

could be used by the N.R.C. to evaluate published or on-going D.O.E. radionuclide transport studies. Curves like those in Figures 1 to 3 can be used to prioritize information needed to identify scenarios or conditions where radioelement speciation must be considered in EPA compliance assessments. These curves can also be used to determine the criteria for the design of laboratory or small-scale field experiments which will yield definitive results for the purposes of waste management.

For example, assume that sorption isotherm data have been obtained for neptunium and that these data are dominated by the behavior of a single species, A. A well-designed sorption experiment should provide reasonable assurance that the isotherm reflects equilibrium conditions. Batch or column tests could be used to determine if species A converts to another species B at a rapid rate (i.e. low value of 1/k). It is possible, however, that true equilibrium is not obtained during tests that are several months long and that, in fact, species A will convert to a more mobile species B during a 10,000 year regulatory period. Such a reaction might also occur in response to changes in the geochemical environment in the aquifer.

This hypothetical conversion of species A to species B could conceivably be detected in very long term (i.e. decades or more) and prohibitively expensive batch or column tests. Curves like those in Figures 1 to 3 could be used to determine the minimum (and cost-effective) durations of tests that are required to produce data that will allow modelers to assure compliance of a repository with the EPA Standard. An example of such an application of the calculations outlined in this letter report is presented below.

Assume that geohydrologic and geochemical data from a repository site suggest that possible values for the retardation factor R_A for a relatively immobile species A of neptunium are less than 200 at the site. If the NRC wishes to use the available sorption data to assure compliance of this site with the EPA Standard, then it must be shown that the reaction rate constant k for the conversion of A to a more mobile species B is less than 1/20 yr^{-1}. Figure 1 shows that if 1/k > 20 years then the conversion of species A to a more mobile species B will not cause the EPA release limit for Np-237 to be exceeded at the site if the conditions describing the source term, waste isolation time and ground-water travel time described in the figure caption are met. Figure 1 also shows that if the lower limit for R_A at the site is equal to 100 then it must be demonstrated that the mean lifetime of A (i.e. 1/k) is greater than 70 years. The duration and design of an experiment required to determine a mean lifetime (1/k) of 70 years for an aqueous complex may be quite different from that required to measure a mean lifetime of 20 years. Thus, curves like those in Figure 1 can be used to evaluate or design the required speciation, transport and reaction kinetics experiments.

E. Recommendations for Future Work

The equations developed in Section D and in the Appendix cannot be applied to all the radionuclides in a high level waste repository. Terms for radioactive decay and production, the existence of several nuclides for a given element, reversible reactions and nonlinear sorption need to be considered in a general treatment of this problem. The particular chemistry of each radionuclide must be considered and an appropriate set of equations must be derived and solved.

The treatment presented thus far has dealt with a single radionuclide. The performance measure used to limit the discharge of a radionuclide in this derivation has been W_i, the EPA Release Limit (40CFR91) for the radionuclide. The EPA Standard, however, regulates the releases of all radionuclides by limiting the permissible value of the EPA release ratio, RR

$$RR = \sum_{i}^{n} \text{Discharge } i/W_i \qquad (8)$$

where the summation is performed over all n radionuclides in the repository. The value of the release ratio must be less than or equal to 1.0 for reasonably foreseeable events. The EPA standard could be violated even if the discharge of each radionuclide is below its EPA release limit. The curves for ^{237}Np presented in Figures 1 to 3 can be used to quantitatively assess compliance with the EPA standard only if discharges of all other radionuclides are zero or negligible.

For real sites, radionuclide discharge may be dominated by one or two elements (cf. Pepping, et al., 1983; Siegel and Chu, 1983). Under these conditions the limitation described above may not be that important. Future calculations should treat this issue in more detail. The sensitivity of the curves with respect to discharge of other radionuclides must be assessed.

Table 1

Classifications of Reactions Important to Radioelement Speciation

Category	Possible Types	Example or Explanation*
Equilibria	1. Irreversible	Products are removed from reaction system
	2. Reversible	Reaction products are not removed from system
Kinetics	1. First order	$UO_2^{+2} + CO_3^{-2} \rightarrow UO_2CO_3^{o}$
	2. n^{th} order	nPu(IV) → Pu(IV) polymer
Retention due to adsorption and/or ion exchange	1. Strongly sorbed species converts to weakly sorbed species	$PuO_2^{+} + OH^{-} \rightarrow PuO_2OH^{o}$
	2. Weakly sorbed species converts to strongly sorbed species	$Pb(OH)_2^{o} \rightarrow PbOH^{+} + OH^{-}$

*Examples are highly speculative. Few data are available for reaction kinetics or retardation factors for species listed.

Table 2

Inventory of Reference Repository
(Spent Fuel From 46,800 MTHM)

Radionuclide	Half-Life (yr)	Curies
^{240}Pu	6.76E3	2.1E7
^{236}U	2.39E7	1.0E4
^{232}Th	1.41E10	1.7E-5
^{228}Ra	6.7	4.7E-6
^{245}Cm	8.27E3	8.4E3
^{241}Pu	14.6	3.2E9
^{241}Am	433.	7.5E7
^{237}Np	2.14E6	1.5E4
^{233}U	1.62E5	1.8
^{229}Th	7300.	1.3E-3
^{246}Cm	4710.	1.6E3
^{242}Pu	3.79E5	7.5E4
^{238}U	4.51E9	1.5E4
^{238}Pu	89.	9.4E7
^{234}U	2.47E5	3.5E3
^{230}Th	8.E4	0.19
^{226}Ra	1600.	3.5E-4
^{210}Pb	21.	3.3E-5
^{243}Am	7650.	6.6E5
^{239}Pu	2.44E4	1.4E7
^{235}U	7.1E8	7.5E2
^{231}Pa	3.25E4	0.25
^{227}Ac	21.6	5.2E-2
^{99}Tc	2.14E5	6.1E5
^{129}I	1.6E7	1.5E3
^{126}Sn	1.0E5	2.2E4
^{90}Sr	28.9	2.4E9
^{14}C	5730.	3.5E4
^{135}Cs	2.0E6	1.3E4
^{137}Cs	30.	3.5E9

Table 3

Initial Inventory of Selected Actinides in Reference Repository (Spent Fuel from 46,800 MTHM)

Element	Nuclide	Half-Life (yr)	Curies	Moles	Total (moles)
Pu	238	89	9.4E7	2.34E4	
Pu	239	2.44E4	1.4E7	9.56E5	
Pu	240	6.76E3	2.1E7	3.97E5	
Pu	241	14.6	3.2E9	1.31E5	
Pu	242	3.79E5	7.5E4	7.96E4	
Pu					1.59E6
U	233	1.62E5	1.8	8.2E-1	
U	234	2.47E5	3.5E3	2.42E3	
U	235	7.1E8	7.5E2	1.49E6	
U	236	2.39E7	1.0E4	6.69E5	
U	238	4.51E9	1.5E4	1.89E8	
U					1.92E8
Np	237	2.14E6	1.5E4	8.99E4	
Np					8.99E4
Cm	245	8.27E3	8.4E3	1.94E2	
Am	241	433	7.5E7	9.09E4	

Table 4

Classification of Radionuclides Based on Decay and Production During Various Time Periods

Class	Description	Examples
1	Decay significant during 500-year isolation period	^{241}Pu, ^{90}Sr, ^{137}Cs, ^{238}Pu
2	Production significant during 500-year isolation period	^{237}Np, ^{234}U
3	Decay significant during 10,000-year EPA regulatory period	^{14}C, ^{240}Pu
4	Production significant during 10,000-year EPA regulatory period	^{236}U
5	Decay not important during 10,000-year EPA regulatory period	^{237}Np, ^{236}U ^{238}U, ^{235}U

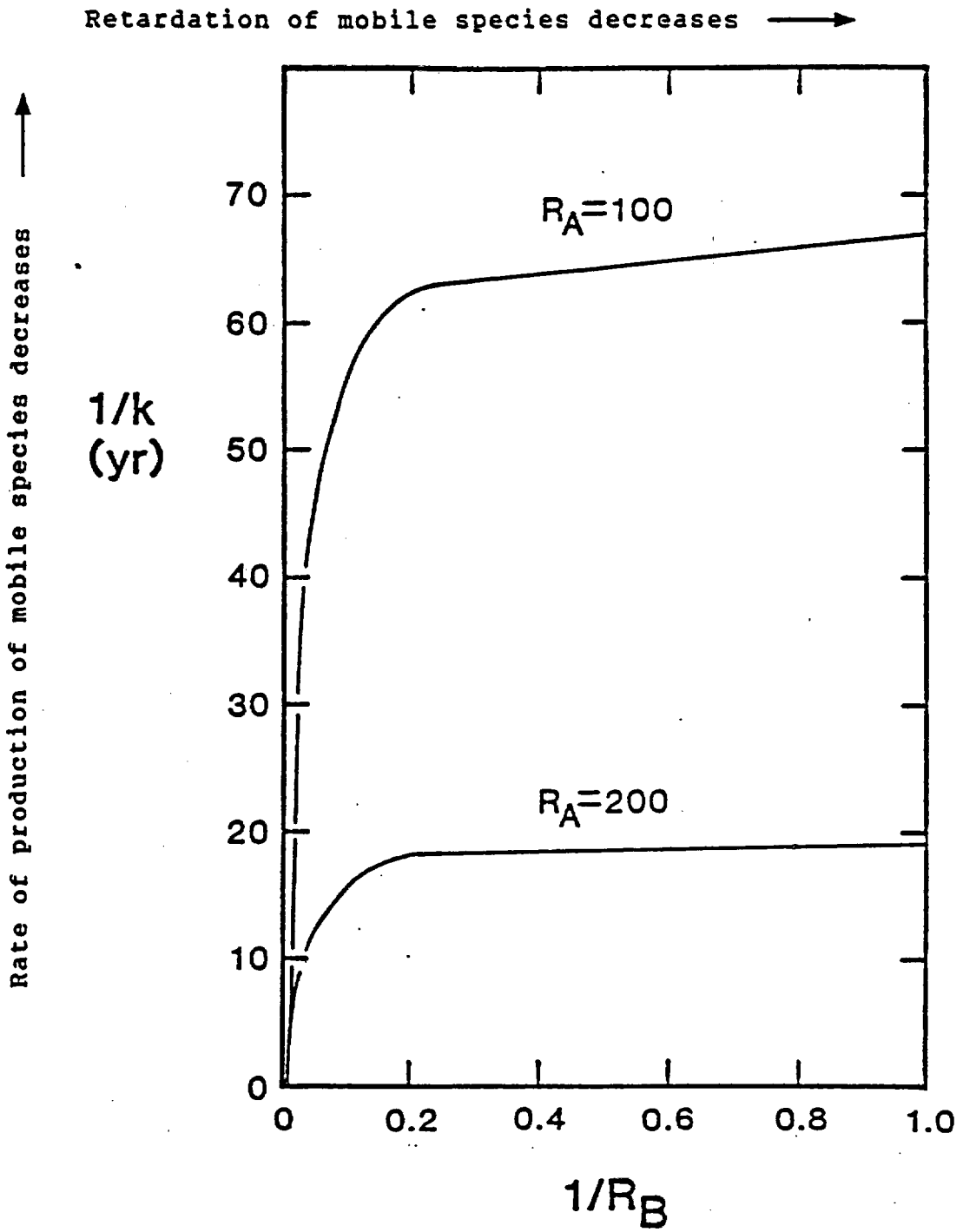

Figure 1. Combinations of values of reaction rate constant k and retardation factor R_B of mobile species B_i which lead to discharge of Np-237 equal to EPA release limit. Curves for two values of retardation factor R_A of immobile species A_i are shown. Ponts below the curves indicate violation of EPA Standard. Source term QA_i^o = 1.0 mole/yr; ground-water travel time x/v = 50 yr; containment period = 1,000 yr; EPA release limit = 20 curies (120 moles Np-237) per kiloton of heavy metal.

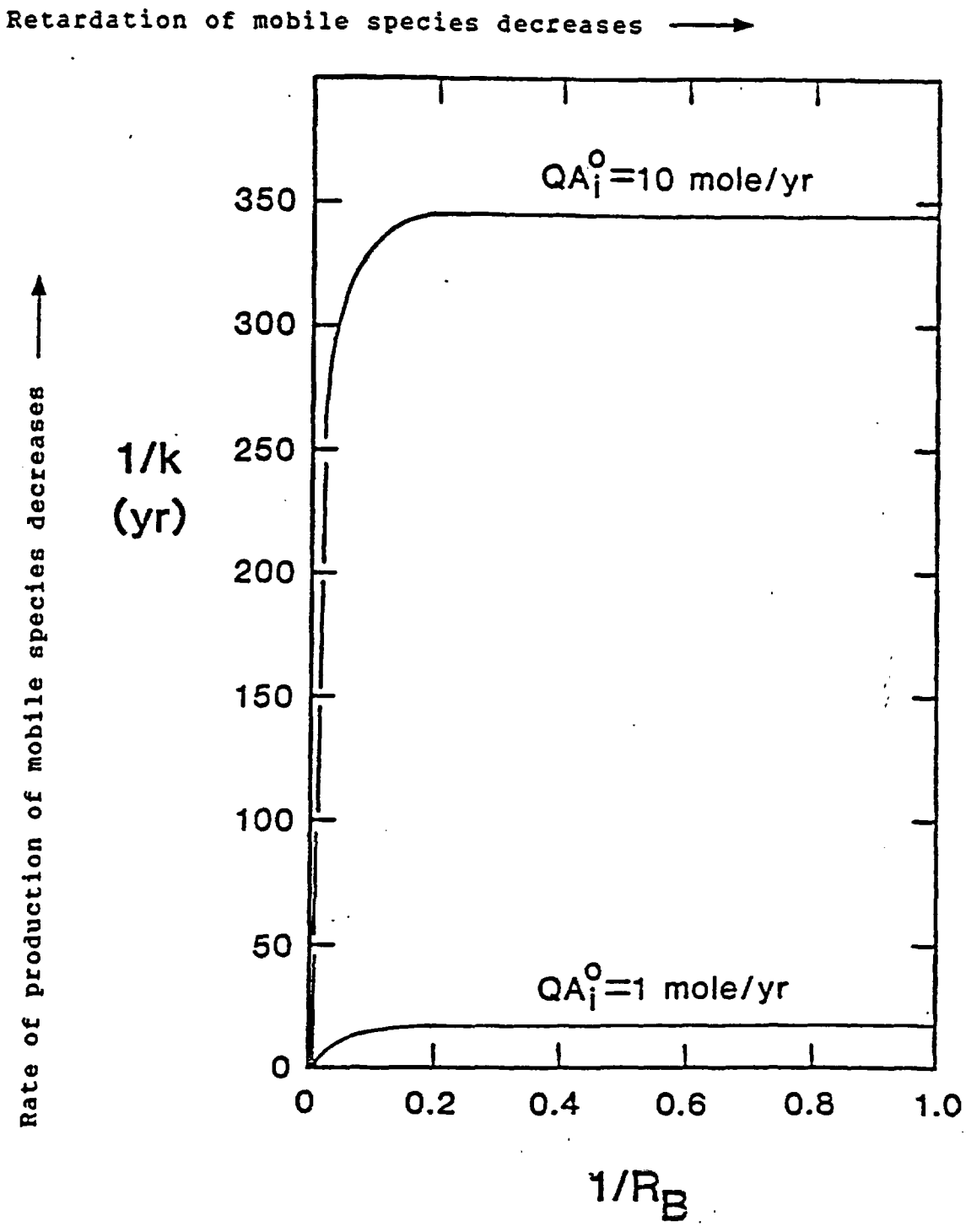

Figure 2. Combinations of values of reaction rate constant k and retardation factor R_B of mobile species B_i which lead to discharge of Np-237 equal to EPA release limit. Curves for two values of the source term QA_i^o are shown. Points below the curves indicate violation of EPA Standard. Retardation factor R_A = 200; ground-water travel time x/v = 50 yr; containment period = 1,000 yr; EPA release limit = 20 curies (120 moles Np-237) per kiloton of heavy metal.

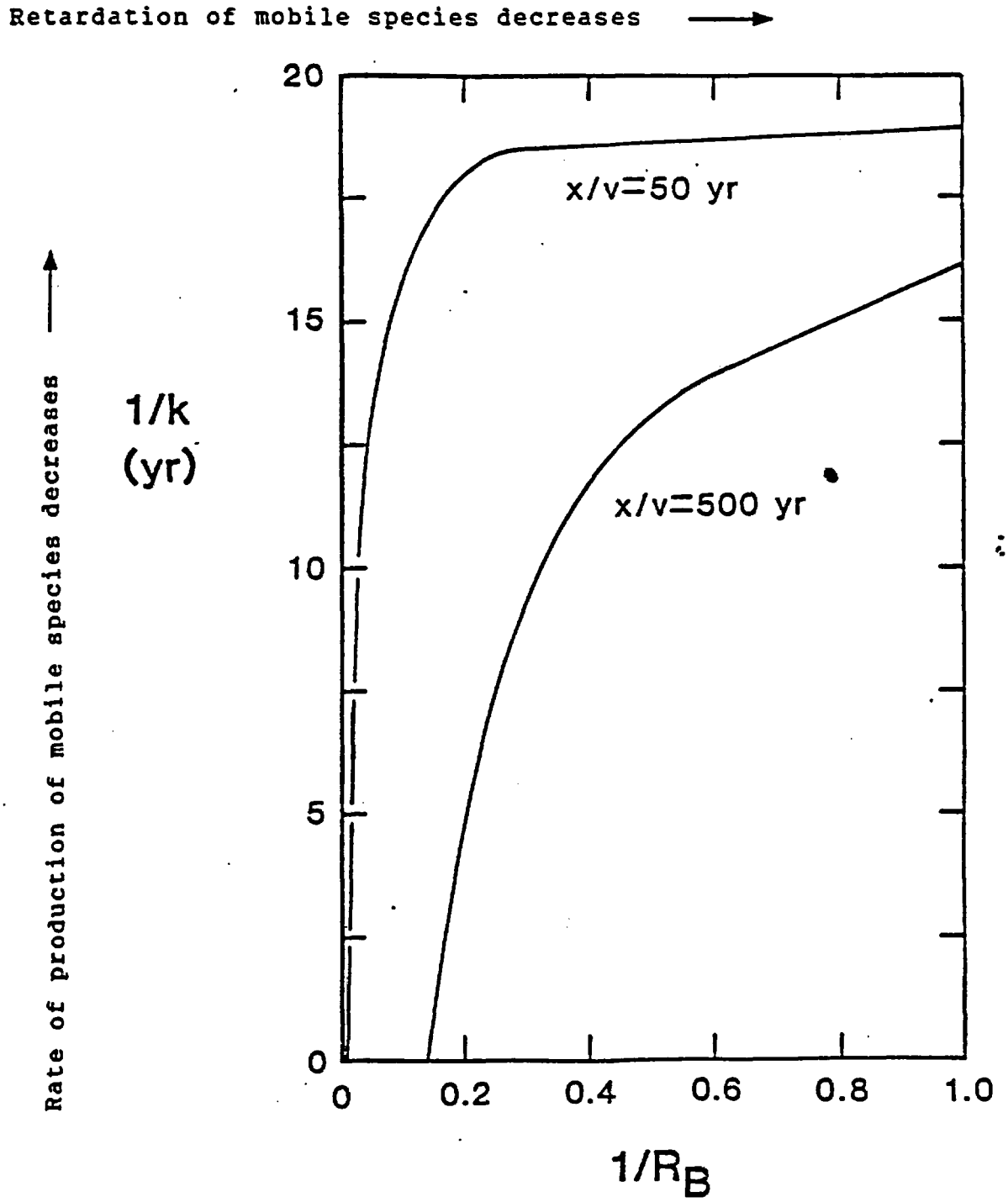

Figure 3. Combinations of values of reaction rate constant k and retardation factor R_B of mobile species B_i, which lead to discharge of Np-237 equal to EPA release limit. Curves for two values of groundwater travel time x/v are shown. Points below the curves indicate violation of EPA Standard. Retardation factor R_A = 200; source term QA_i^o = 1.0 mole/yr; containment period = 1,000 yr; EPA release limit = 20 curies (120 moles Np-237) per kiloton of heavy metal.

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APPENDIX

Convective Radionuclide Transport With Local Sorption Equilibrium and First-Order, Irreversible Chemical Reaction

Let A and B denote two different chemical species of the same radionuclide i, and let L denote some reactant (ligand) which exists in an approximately constant concentration in the flowing fluid. Further, let sorption of species A and B by the rock matrix occur by reversible processes such as adsorption or ion exchange; let local sorption equilibrium exist between the flowing fluid and rock matrix, and let solution-phase radionuclide concentrations be sufficiently dilute so that sorption equilibrium isotherms are linear. Then consider an irreversible reaction such as

$$A + L \xrightarrow{k_i} B$$

which occurs in the flowing fluid. Let the rate of the above reaction be at least approximately first order, that is

$$r_A = k_i C_A C_L = k C_A = r_B$$

where r_A and r_B represent the rate of depletion of species A and rate of production of species B, respectively. If nuclide i is initially present in the inventory but is not subsequently produced as a daughter product, then the material balances for one-dimensional transport of species A and B in a homogeneous, saturated porous medium are, respectively,

$$\frac{\partial C_A}{\partial t} + v \frac{\partial C_A}{\partial x} = - \frac{1}{m} \frac{\partial q_A}{\partial t} - kC_A - \lambda C_A - \frac{\lambda}{m} q_A \qquad \text{(A1)}$$

$$\frac{\partial C_B}{\partial t} + v \frac{\partial C_B}{\partial x} = - \frac{1}{m} \frac{\partial q_B}{\partial t} + kC_A - \lambda C_B - \frac{\lambda}{m} q_B \qquad \text{(A2)}$$

where

C_A = concentration of A in solution (mole/cc)
C_B = concentration of B in solution (mole/cc)

m = void ratio = $\phi/(1-\phi)\rho$
ϕ = effective porosity
λ = decay constant for radionuclide i
q_A = concentration of A in solid (mole/cc)
q_B = concentration of B in solid (mole/cc)
v = interstitial fluid velocity
x = direction of fluid flow .

Let

$$R_A = 1 + Kd_A \frac{\rho(1-\phi)}{\phi} = 1 + \frac{q_A}{C_A m} = \text{retardation factor for A}$$

$$R_B = 1 + Kd_B \frac{\rho(1-\phi)}{\phi} = 1 + \frac{q_B}{C_A m} = \text{retardation factor for B}$$

where

Kd_A = sorption equilibrium distribution coefficient for A (cc/gm)
Kd_B = sorption equilibrium distribution coefficient for B (cc/gm)
ρ = grain density .

Then, Equations (A1) and (A2) can be rewritten as:

$$\frac{\partial C_A}{\partial t} + \frac{v}{R_A}\frac{\partial C_A}{\partial x} = -\frac{(k + \lambda R_A)C_A}{R_A} \qquad \text{(A3)}$$

$$\frac{\partial C_B}{\partial t} + \frac{v}{R_B}\frac{\partial C_B}{\partial x} = \frac{kC_A}{R_B} - \lambda C_B \quad . \qquad \text{(A4)}$$

For purposes here, consider the initial conditions

$$C_A(x,0) = 0 \text{ and } C_B(x,0) = 0 \qquad \text{(A5a)}$$

$$q_A(x,0) = 0 \text{ and } q_B(x,0) = 0 \qquad \text{(A5b)}$$

and the boundary conditions

$$C_A(0,t) = A_i^o e^{-\lambda t} \tag{A6a}$$

$$C_B(0,t) = 0 \tag{A6b}$$

where A_i^o = concentration of radionuclide released from repository and depends on solubility and release rate.

Solving Equations (3) and (4) subject to the above initial and boundary conditions gives C_A and C_B at any time t or position x along the flow path as a function of v, k, λ, R_A, and R_B. A solution using the method of Laplace transforms is illustrated below, after which, the resulting expressions for C_A and C_B are integrated to obtain Equation (7).

Let $\bar{C}_A$ and $\bar{C}_B$ denote the Laplace transforms of C_A and C_B with respect to t. That is

$$\bar{C}_A = L\{C_A\} = \int_0^\infty e^{-st} C_A dt$$

and similarly for $\bar{C}_B$. Then consider the material balance for species A, Equation (A3), which transforms to

$$\frac{d\bar{C}_A}{dx} = -\left(\frac{R_A s + k + \lambda R_A}{v}\right) \bar{C}_A \quad .$$

Then

$$\bar{C}_A = A \exp\left[-\left(\frac{R_A s + k + \lambda R_A}{v}\right) x\right]$$

where A = constant of integration.

From the boundary condition Equation (A6a)

$$\bar{C}_A(x = 0) = \frac{A_i^o}{s+\lambda}$$

and

$$\bar{C}_A = \frac{A_i^o}{s+\lambda} \exp\left(\frac{-kx}{v}\right) \exp\left[\frac{-R_A(s+\lambda)x}{v}\right]$$

Then using the shifting theorem and inverting the Laplace transform $\bar{C}_A$ gives

$$C_A = A_i^o e^{-\lambda t} e^{\frac{-kx}{v}} H(t - R_A x/v)$$

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

Now consider the material balance for species B, Equation (A4) which transforms to

$$\frac{d\bar{C}_B}{dx} + \frac{R_B(s+\lambda)}{v} \bar{C}_B = \frac{k}{v} \bar{C}_A$$

or

$$\frac{d\bar{C}_B}{dx} + \frac{R_B(s+\lambda)}{v} \bar{C}_B$$

$$= \frac{k}{v} \frac{A_i^o}{s+\lambda} \exp\left(\frac{-kx}{v}\right) \exp\left[\frac{-R_A(s+\lambda)x}{v}\right]$$

Solving the above differential equation for $\bar{C}_B$ gives

$$\bar{C}_B = A \exp\left[\frac{-R_B(s+\lambda)x}{v}\right]$$

$$- \frac{A_i^o k}{(s+\lambda)\ (R_A-R_B)(s+\lambda) + k} \exp\left(\frac{-kx}{v}\right) \exp\left[\frac{-R_A(s+\lambda)x}{v}\right]$$

where A is again a constant of integration. Then from the boundary condition Equation (A6b)

$$\bar{C}_B(x = 0) = 0 = A - \frac{A_i^o k}{(s+\lambda)[(R_A-R_B)(s+\lambda) + k]}$$

and

$$\bar{C}_B = \frac{A_i^o k}{(s+\lambda)\ (R_A-R_B)(s+\lambda) + k} \left\{ \exp\left[\frac{-R_B(s+\lambda)x}{v}\right] - \exp\left(\frac{-kx}{v}\right) \exp\left[\frac{-R_A(s+\lambda)x}{v}\right]\right\}$$

Now, using the shifting and convolution theorems to invert the Laplace transform $\bar{C}_B$ gives

$$C_B = A_i^o k \exp(-\lambda t)\left[\int_0^t f_1(\tau)g(t-\tau)d\tau - \exp(-kx/v)\int_0^t f_2(\tau)g(t-\tau)d\tau\right]$$

where $f_1(\tau) = L^{-1}\left\{\frac{\exp(-R_B sx/v)}{s}\right\}$

$$= H\ (\tau-R_B x/v)$$

$$f_2(\tau) = L^{-1}\left\{\frac{\exp(-R_A sx/v)}{s}\right\}$$

$$= H\ (\tau-R_A x/v)$$

$$g(t-\tau) = L^{-1}\left\{\frac{1}{(R_A-R_B)s + k}\right\}$$

$$= \left(\frac{1}{R_A-R_B}\right) \exp\left[\frac{-k(t-\tau)}{R_A-R_B}\right]$$

and L^{-1} F(S) denotes the inverse Laplace transform of F(S). Also, note that

$$\frac{1}{(R_A-R_B)s + k} = \left(\frac{1}{R_A-R_B}\right)\left(\frac{1}{s + \frac{k}{R_A-R_B}}\right) .$$

Evaluating the above integrals gives finally

$$C_B = A_i^o \exp(-\lambda t)\left\{\left[1-\exp\left(\frac{-k(t-R_Bx/v)}{R_A-R_B}\right)\right] H(t-R_Bx/v)\right.$$

$$\left. - \exp(-kx/v)\left[1-\exp\left(\frac{-k(t-R_Ax/v)}{R_A-R_B}\right)\right] H(t-R_Ax/v)\right\}$$

or,

$$C_B = 0 \text{ for } t < R_Bx/v < R_Ax/v$$

$$C_B = A_i^o e^{-\lambda t}\left[1-\exp\left(\frac{-k(t-R_Bx/v)}{R_A-R_B}\right)\right]$$

for $R_Bx/v < t < R_Ax/v$ (i.e., $R_A > R_B$)

$$C_B = -A_i^o e^{-\lambda t}\, e^{-kx/v}\left[1-\exp\left(\frac{-k(t-R_Ax/v)}{R_A-R_B}\right)\right]$$

for $R_Ax/v < t < R_Bx/v$ (i.e., $R_A < R_B$)

$$C_B = A_i^o e^{-\lambda t}\left[1-\exp\left(\frac{-k(t-R_B x/v)}{R_A-R_B}\right)\right]$$

$$-A_i^o e^{-\lambda t}\, e^{-kx/v}\left[1-\exp\left(\frac{-k(t-R_A x/v)}{R_A-R_B}\right)\right]$$

for $t > R_B x/v$ and $t > R_A x/v$.

Now, if W_i denotes the EPA release limit for radionuclide i, then for compliance with the EPA Standard, the integrated discharge of radionuclide i must not exceed W_i, or

$$\int_0^{t^*} Q(C_A + C_B)dt \le W_i$$

where t* is the portion of EPA regulatory period following the isolation period and where Q is the fluid discharge rate. From above, with $\lambda \approx 0$

$$C_A + C_B = A_i^o\left\{1-\exp\left[\frac{-k(t-R_B x/v)}{R_A-R_B}\right] H(t-R_B x/v)\right\}$$

$$+ A_i^o \exp(-kx/v)\exp\left[\frac{-k(t-R_A x/v)}{R_A-R_B}\right] H(t-R_B x/v)$$

For constant Q, $t > R_B x/v$, and $t > R_A x/v$, evaluation of the preceding integral gives

$$W_i \ge QA_i^o\left[t^* - R_B x/v + \frac{R_A - R_B}{k}\left[\exp\left(\frac{-k(t^* - R_B x/v)}{R_A - R_B}\right) - 1\right]\right]$$

$$+ QA_i^o \exp(-kx/v)\left[\frac{(R_A - R_B)}{k}\right]\left[1 - \exp\left(\frac{-k(t^* - R_A x/v)}{R_A - R_B}\right)\right]$$

which is Equation (7).