

**AN IMPROVED METHOD FOR MODELING SORPTION OF
RADIONUCLIDES DURING LIQUID PHASE TRANSPORT FOR
PERFORMANCE ASSESSMENTS OF HIGH-LEVEL WASTE
REPOSITORIES**

Mark S. Jarzempa

The Center for Nuclear Waste Regulatory Analyses

Southwest Research Institute

6220 Culebra Road

San Antonio, TX 78238-5166

Telephone: (210) 522-6828

Fax: (210) 522-5155

Internet: mjarzempa@smtp.cnwra.swri.edu

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AN IMPROVED METHOD FOR MODELING SORPTION OF RADIONUCLIDES DURING LIQUID PHASE TRANSPORT FOR PERFORMANCE ASSESSMENTS OF HIGH-LEVEL RADIOACTIVE WASTE REPOSITORIES

ABSTRACT

An improved model (over a simple "retardation factor" approach) to account for the effects of radionuclide sorption (adsorption plus ion-exchange) on geologic media during liquid phase transport of the radionuclides from a high-level radioactive waste (HLW) repository is presented in this paper. The improved model has the ability to account for: (i) the competitive nature of radionuclide sorption, (ii) the reduction of the number of available sorber sites on the sorbent media due to occupation of the adsorption sites, and (iii) radionuclide sorption on partially saturated geologic media. The improved model was applied to a hypothetical system composed of ^{238}U , ^{239}Pu , water, and saturated rock typical of Yucca Mountain, Nevada, where the rock was assumed, for simplicity, to exhibit only the adsorption property. The results of the improved model of this system were compared to the results obtained from modeling this system using a simple constant retardation factor approach, both models using available batch sorption data. It was found that the new, more robust model predicted groundwater ^{239}Pu concentrations that were about three orders of magnitude higher at a distance of 5,000 m into the saturated geologic media. This difference suggests that the constant retardation factor approach may be nonconservative. The difference was due to ^{238}U and ^{239}Pu occupying a significant number of the available adsorption sites on the media thus allowing the ^{239}Pu to pass through the medium unimpeded by sorption. The improved model could account for this effect whereas the constant retardation factor model could not. This suggests that failure to account for the competitive nature of sorption could produce misleading performance assessment (PA) predictions

since in actuality, radionuclides will be competing with each other as well as with naturally occurring ions. The effect of competition will be even greater than is shown in this paper. It is proposed that the improved, readily incorporated model be used for PAs of HLW repositories to account for the effects of radionuclide sorption during liquid phase transport of radionuclides away from HLW containers.

INTRODUCTION

One of the most difficult processes to accurately model in the PA of HLW repositories (1,2,3,4) is the sorption (adsorption plus ion-exchange) of radionuclides, dissolved in groundwater flowing through the repository, onto surrounding geologic media. Current modeling approaches use a retardation factor (R_f) that is defined as the ratio of the groundwater travel velocity to the radionuclide travel velocity. This factor is generally assumed to be independent of the radionuclide groundwater concentration and sorbed population density. The difference between the two velocities is due to radionuclide sorption and subsequent desorption along the transport path. While it is known from both theory and experiment that the sorption properties of media are not independent of the fluid species concentrations, solution chemistry, or sorbed population density, these assumptions have been made because there currently exists no better "tractable" model to incorporate their effects on sorption processes for use in PA models.

Using a simple retardation factor has the following disadvantages:

- (i) As stated, the retardation factor approach does not take into account the competitive effect of sorption. This effect is due to the filling of sorber sites for one radionuclide by another radionuclide, that is, if a sorber site is occupied by an atom of uranium, then the sorber site is no longer available to sorb plutonium.
- (ii) The retardation factor can be difficult to determine for partially saturated media.
- (iii) Using a constant retardation factor may not adequately represent the effects of system chemistry (i.e., variations in sorption parameters with pH) (5).

In (6), modeling was presented that accounted for the competitive effects of sorption of dissolved species on saturated media and compared to experiment with good agreement. The model used in (5), however, did not account for many processes such as: dynamic effects, radioactive decay of the radionuclides, partial saturation of the media, chemical reaction in the water and ingrowth of radionuclides from parent decays. The model used by (6,7) to describe adsorption was modified from a model originally developed by (8) and later modified by (9). In this model, partial differential equations were derived for the concentration of atomic species in both the adsorbed state as well as the "free" or fluid bound state in a differential volume of a porous medium, assuming that a Langmuir isotherm accurately characterizes the adsorption process. In (6), ion-exchange with the media was modeled as an independent process from the adsorption process.

The purpose of this paper is to describe a model, based on the conservation of atoms, to be used in PAs of HLW repositories. Specifically, it is the authors intent that the new model described herein should be tested for application in conducting PAs for Yucca Mountain, the nation's proposed HLW geologic repository. Such application will require estimation of some of the model parameters through sorption experiments. This model is based on a Langmuir Isotherm for modeling the adsorption process, and a first order rate law for modeling ion-exchange. This model will be used in this paper to predict sorption of radionuclides from groundwater onto geologic media with given sorption characteristics. These predictions will be compared to calculations made using a simple constant retardation factor. The comparison will show significant differences between predictions made by the two modeling approaches. The modeling presented in this paper is based on the assumption, as was done in (5), that ion-exchange and adsorption occur independently.

ANALYSIS

The ultimate goal of sorption analyses for PAs is to predict groundwater concentrations of radionuclide contaminants at some point along the transport path, perhaps the accessible environment.

This goal can be accomplished by solving a set of coupled partial differential equations for the groundwater radionuclide concentration as a function of time and space in the geologic media. To derive these partial differential equations, one must consider the radionuclide input and output to the groundwater in a differential volume in the media. An example of this differential volume is shown in Figure 1. The differential volume of Figure 1 is composed of rock with a given porosity that is partially (or perhaps totally) saturated with water. Water is assumed to flow uniformly through the differential volume with some velocity that is due to a mixture of gravitational and capillary potential against some flow resistance. The physics and subsequent equations that govern this process are understood and are described elsewhere (10,11,12). For the purposes of the model described in this paper, it is assumed that the magnitude and direction of this flow is known. The partial differential equation for the concentration of radionuclide species i (the term "species" denotes that the same radionuclide could exist in different chemical forms) in the groundwater as a function of position and time is:

$$\begin{aligned} \frac{\partial}{\partial t} c_i(\vec{r}, t) = & \frac{\lambda_i^C}{\epsilon s(\vec{r}, t)} n_i^c(\vec{r}, t) + \left\{ \sum_j k_{j \rightarrow i}^E [c_j(\vec{r}, t)]^{v_j} [q_i^c(\vec{r}, t)]^{v_j} \right\} - \lambda_i^P c_i(\vec{r}, t) + \sum_j \lambda_{j \rightarrow i}^P c_j(\vec{r}, t) \\ & - \sum_k R_{i \rightarrow k} c_i(\vec{r}, t) + \sum_j R_{j \rightarrow i} c_j(\vec{r}, t) - \frac{(k_i^0)'}{\epsilon} \left[1 - \frac{\sum_j n_j^c(\vec{r}, t)}{s(\vec{r}, t) n_T(\vec{r}, t)} \right] c_i(\vec{r}, t) - \left\{ \sum_j k_{i \rightarrow j}^E [q_i^c(\vec{r}, t)]^{v_i} [c_j(\vec{r}, t)]^{v_j} \right\} \\ & - \vec{\nabla} \cdot [\vec{U}(\vec{r}, t) c_i(\vec{r}, t)] + \vec{\nabla} \cdot (D_i(\vec{r}, t) \vec{\nabla} c_i(\vec{r}, t)) \end{aligned} \quad (1)$$

where the coefficients in Equation (1) are (in order of appearance):

$c_i(\vec{r}, t)$ = The groundwater concentration of radionuclide species i (number of atoms per liquid volume $\frac{\#}{L^3}$).

λ_i^C = The desorption (de-adsorption) or "chemical decay" coefficient for radionuclide species i , [chemical decay refers to the fact that the radionuclide is changing its chemical state (free versus adsorbed) and not its physical state, as is the case with radioactive decay] (per unit time $\frac{1}{T}$).

ϵ = The rock porosity equals the volume of pore space per unit total volume.

$s(\vec{r}, t)$ = The saturation fraction equals the fraction of the pore space that is filled with water. This approximates, to first order, the fraction of adsorber sites that are covered with groundwater.

$n_i^C(\vec{r}, t)$ = The number of atoms of radionuclide species i that are adsorbed to rock surfaces that are covered with water at time t , per unit total volume (volume of rock plus pores) (number of atoms per total volume $\frac{\#}{L^3}$).

$k_{j \rightarrow i}^E$ = The ion-exchange rate constant for radionuclide species j substituting for radionuclide species i .

$q_i^C(\vec{r}, t)$ = The number of radionuclide species i that are bound to the rock surfaces through an ionic bond and are covered with water at time t per unit total volume (number of atoms per total volume $\frac{\#}{L^3}$).

λ_i^P = The radioactive or physical decay constant for radionuclide species i (per unit time $\frac{1}{T}$).

- $\lambda_{j \rightarrow i}^P$ = The radioactive or physical decay constant for radionuclide species j that results in the production of radionuclide species i (per unit time $\frac{1}{T}$).
- $R_{i \rightarrow k}$ = The reaction rate of radionuclide species i with other groundwater constituents that results in the production of radionuclide species k (per unit time $\frac{1}{T}$).
- $(k_i^0)'$ = The number of atoms of radionuclide species i adsorbed per unit total volume per unit time per unit concentration of radionuclide species i in the groundwater, in the absence of any adsorbed atoms on the rock surfaces (per unit time $\frac{1}{T}$).
- $n_T(\vec{r})$ = The number of adsorber sites of one type per unit total volume (number per unit total volume $\frac{1}{L^3}$).
- v_i = The valence of radionuclide species i .
- $\vec{U}(\vec{r}, t)$ = The pore velocity of the interstitial fluid (water) as a function of position and time (length per unit time $\frac{L}{T}$).
- $D_i(\vec{r}, t)$ = The diffusion coefficient of radionuclide species i in the media as a function of position and time (length squared per unit time, $\frac{L^2}{T}$) = $f[\epsilon, \tau, S(\vec{r}, t)] \cdot D_{wi}$, where; $f[\epsilon, \tau, S(\vec{r}, t)] = a$

function of the listed parameters, τ = the tortuosity of the media, and D_{wi} = the diffusion coefficient of radionuclide species i in water.

\vec{r} = Space coordinate vector.

t = Time.

The physical processes that the terms in Equation (1) describe are as follows: The first term describes the ingrowth of radionuclide species i from desorption of adsorbed species i that are covered with water, assuming that only one type of adsorber site exists. The second term describes the ingrowth of radionuclide species i in the groundwater from ion-exchange with some other chemical species that is ionically bound to the rock surface. It is assumed that this process can be accurately described by a first order approximation and that adsorption and ion-exchange occur independently of each other. These are the same assumptions that were used in (7) and the authors found good agreement of their model with experiment, therefore the same assumptions are used here. The third term describes the radioactive decay of radionuclide species i in the groundwater. The fourth term describes the ingrowth of radionuclide species i from radioactive decay of parent nuclei. The fifth and sixth terms describe the ingrowth and outgrowth of radionuclide species i due to chemical reaction in the groundwater. The seventh term describes losses from the groundwater due to adsorption on the media. The eighth term describes losses from the groundwater due to ion-exchange of radionuclide species i with some chemical species on the media. The ninth and tenth terms describe the motion of radionuclide species i in the groundwater due to advection and dispersion, respectively.

Since both $n_i^c(\vec{r},t)$ and $q_i^c(\vec{r},t)$ appear in Equation (1) it is also necessary to track both of these quantities. Equation (2) is the partial differential equation for $n_i^c(\vec{r},t)$:

$$\begin{aligned}
\frac{\partial}{\partial t} n_i^c(\vec{r}, t) = & (k_i^0)' \cdot s(\vec{r}, t) \left[1 - \frac{\sum_j n_j^c(\vec{r}, t)}{s(\vec{r}, t) n_T(\vec{r})} \right] c_i(\vec{r}, t) + \sum_j \lambda_{j \rightarrow i}^P n_j^c(\vec{r}, t) \\
& - \lambda_i^P n_i^c(\vec{r}, t) - \lambda_i^C n_i^c(\vec{r}, t) \\
& + \frac{\partial}{\partial t} s(\vec{r}, t) \cdot F
\end{aligned} \tag{2}$$

where

$$F = \frac{n_i^u(s, \vec{r}, t)}{1 - s(\vec{r}, t)} \quad \text{if } \frac{\partial}{\partial t} s(\vec{r}, t) \geq 0$$

$$F = \frac{n_i^c(\vec{r}, t)}{s(\vec{r}, t)} \quad \text{if } \frac{\partial}{\partial t} s(\vec{r}, t) < 0$$

The two definitions of F describe the covering and uncovering of adsorbed species, where $n_i^u(\vec{r}, t)$ is the number of atoms of radionuclide species i that are sorbed to rock surfaces and are no longer covered with water per unit total volume. These atoms are not available for sorption until the surface is again covered by water. The introduction of this new quantity necessitates its tracking. Equation (3) is the time rate of change partial differential equation for $n_i^u(\vec{r}, t)$:

$$\begin{aligned}
\frac{\partial}{\partial t} n_i^u(s', \vec{r}, t) &= \sum_j \lambda_{j \rightarrow i}^P n_i^u(s', \vec{r}, t) - \lambda_i^P n_i^u(s', \vec{r}, t) \\
&\quad - \frac{\partial}{\partial t} s(\vec{r}, t) \cdot F \cdot \delta[s' - s(\vec{r}, t)] \quad s' \geq s(\vec{r}, t) \\
n_i^u(s', \vec{r}, t) &= 0 \quad s' < s(\vec{r}, t)
\end{aligned} \tag{3}$$

where s' is saturation values other than the saturation value s at time t and δ is the kronecker delta function. Equation (1) introduced another quantity, $q_i^c(\vec{r}, t)$. The time rate of change partial differential equation describing this quantity is:

$$\begin{aligned}
\frac{\partial}{\partial t} q_i^c(\vec{r}, t) &= \left\{ \sum_j k_{i \rightarrow j}^E [q_j^c(\vec{r}, t)]^{\nu_i} [c_i(\vec{r}, t)]^{\nu_j} \right\} + \sum_j \lambda_{j \rightarrow i}^P q_j^c(\vec{r}, t) - \lambda_i^P q_i^c(\vec{r}, t) \\
&\quad - \left\{ \sum_j k_{j \rightarrow i}^E [q_i^c(\vec{r}, t)]^{\nu_j} [c_j(\vec{r}, t)]^{\nu_i} \right\} \\
&\quad + \frac{\partial}{\partial t} s(\vec{r}, t) \cdot G
\end{aligned} \tag{4}$$

where

$$\begin{aligned}
G &= \frac{q_i^u(s, \vec{r}, t)}{1 - s(\vec{r}, t)} \quad \text{if } \frac{\partial}{\partial t} s(\vec{r}, t) \geq 0 \\
G &= \frac{q_i^c(\vec{r}, t)}{s(\vec{r}, t)} \quad \text{if } \frac{\partial}{\partial t} s(\vec{r}, t) < 0
\end{aligned}$$

In Equation (4), similarly to Equation (2), the water uncovered, ionically bound species population, $q_i^u(\vec{r}, t)$ is introduced. The time rate of change partial differential equation for this quantity is:

$$\begin{aligned}
\frac{\partial}{\partial t} q_i^u(s', \vec{r}, t) &= \sum_j \lambda_j^p q_i^u(s', \vec{r}, t) - \lambda_i^p q_i^u(s', \vec{r}, t) \\
&\quad - \frac{\partial}{\partial t} s(\vec{r}, t) \cdot G \cdot \delta[s' - s(\vec{r}, t)] \quad s' \geq s(\vec{r}, t) \\
q_i^u(s', \vec{r}, t) &= 0 \quad s' < s(\vec{r}, t)
\end{aligned} \tag{5}$$

The model described by Equations (1) through (5) does not account for precipitation of radionuclide species or dissolution of radionuclides in solid phases (i.e., one assumes that the interaction of species with the media is strictly a surface phenomenon), nor does it account for any exchange of radionuclide species i from the groundwater to the air space above the water in the pore and hence any sorption of radionuclides in the gaseous state. Also, because competition with naturally occurring ions could be important as well, the concentrations of naturally occurring (nonradionuclide species) ions should also be tracked.

It should be noted that many of the parameters in the above equations are presented as "constants." For example, the chemical reaction constants could be functions of the concentration of whatever radionuclide species i is reacting with. However, without going into the specific reactions, these "constants" would be difficult to quantify and beyond the scope of this paper. It is anticipated that the parameters used in the above equations could be functions of solution characteristics, such as pH (13,14). Also, an alternative to the assumption of a monolayer of adsorbing species could be the introduction of a second type of adsorber site, say type 2 adsorber sites, into the differential equations to account for multilayer adsorption. These type 2 sorber sites are created by the sorbed species population being polarized by the surface charge of the original geologic media and, therefore, the adsorption parameters describing these new adsorption sites would be different from the ones used to describe the geologic media and would also be functions of the adsorbed population density. This type

of modification, however, would further complicate the model, and it appears that, except at very high surface loadings, a monolayer assumption describes the situation fairly accurately (14). It has also been assumed in Eqs. (1) through (5) that only one type of sorber site exists on the mineral surface.

The new model has the ability to accommodate the competitive nature of radionuclide sorption. Simply stated, competitive sorption means that any sorbed radionuclide has the ability to block a sorption site from use by another radionuclide. This creates, in essence, a decrease in the amount of available sorber sites. Another important feature of this improved model is that it has the ability to model sorption for spatially variable flow regimes. The flow velocity term in Equation (1) can be a function of position, thus increased or decreased flow of groundwater and, hence, retardation of radionuclides in rock fractures could be accounted for.

Upon initial examination, Equations (1) through (5) appear very complex. It is anticipated that these equations would be solved numerically along with the groundwater flow equations. Many of the constants in the equations will be zero. For example the radioactive decay constants resulting in the production of a particular daughter (λ_{j-i}^P) would be nonzero for perhaps only one or two parent isotopes. This fact will simplify the model greatly when it is solved numerically. Alternatively, further assumptions could be made to directly simplify Equations (1) through (5). For example, if it is assumed that steady-state exists (i.e., no importance of the water uncovered sorbed population density), that there is no ingrowth of radionuclides from parent radioactive decay, that chemical reaction in the groundwater can be neglected and that the retardation process is dominated by adsorption (i.e., ion-exchange is negligible), then Equation (1) becomes:

$$0 = \left[\frac{\lambda_i^C}{\epsilon} - \frac{\lambda_i}{\epsilon \cdot S(\vec{r}, t)} \right] \left[\frac{\frac{(k_i^0)'}{\lambda_i} S(\vec{r}, t) \cdot c_i(\vec{r})}{1 + \frac{1}{n_T(\vec{r})} \sum_j \frac{(k_j^0)'}{\lambda_j} c_j(\vec{r})} \right] - \lambda_i^P c_i(\vec{r}) \quad (6)$$

$$- \vec{\nabla} \cdot [U(\vec{r}) c_i(\vec{r})] + \vec{\nabla} \cdot D_i(\vec{r}) \vec{\nabla} c_i(\vec{r})$$

which is much more manageable for PA calculations. One should note from Equation (6) that the denominator of the term in square brackets on the right-hand side describes the competitive effects of sorption and neglecting this term, as will be shown, could have adverse consequences for predictions of groundwater radionuclide concentration calculations. One will also note that Equation (6) is now only a function of the competing species groundwater concentrations and not of the sorbed species population density, thus extensively simplifying the model. Another interesting result is obtained if one considers the definition of K_d as given in Appendix A. Substituting Equation (A-3) into Equation (6) yields:

$$0 = \left[\frac{\lambda_i^C}{\epsilon} - \frac{\lambda_i}{\epsilon S(\vec{r}, t)} \right] \left[\frac{\rho_b K_d^i S(\vec{r}, t) \cdot c_i(\vec{r})}{1 + \frac{\rho_b}{n_T(\vec{r})} \sum_j K_d^j c_j(\vec{r})} \right] \quad (7)$$

$$- \lambda_i^P c_i(\vec{r}) - \vec{\nabla} \cdot [\vec{U}(\vec{r}) c_i(\vec{r})] + \vec{\nabla} \cdot D_i(\vec{r}) \vec{\nabla} c_i(\vec{r})$$

As is the case with any model, simplifications can be made provided there is justification for the simplifications. In general, the most robust model, as given by Equations (1) through (5), could be simplified in any manner that the investigator deems appropriate.

SIGNIFICANCE

As an example of the significance of this way of accounting for radionuclide sorption in

transport, consider a one dimensional system, composed of ^{238}U (radionuclide 1), ^{239}Pu (radionuclide 2), water, and rock where it is assumed that: (i) a steady-state exists, (ii) radioactive ingrowth of radionuclides is negligible, (iii) chemical reaction in the groundwater is negligible, (iv) the media exhibit only the adsorption property for uranium and plutonium ions, and (v) diffusion of radionuclides in the water is negligible. A comparison is made in this section of the groundwater plutonium concentration as a function of distance into the media as calculated by a simple constant retardation factor model and the new model.

GROUNDWATER PLUTONIUM CONCENTRATIONS CALCULATED USING CONSTANT RETARDATION FACTORS

The method currently used for calculating the concentration of plutonium in the groundwater at some point along the transport path is to assume that the radionuclide travels with some constant, reduced velocity (as compared to the groundwater travel velocity), independent of sorbed radionuclide populations, that is due to the effects of sorption. The ratio of the groundwater travel velocity to the radionuclide travel velocity is called the retardation factor. Under this type of modeling the concentration of a radionuclide in the groundwater at some point along the travel path in steady-state is given by:

$$c_2(x) = c_{2,0} \exp \left[-\lambda_2^P \cdot R_f^{Pu} \cdot t_w(x) \right] \quad (8)$$

where:

$c_{2,0}$ = The concentration of plutonium in the groundwater at $x=0$.

R_f^{Pu} = The retardation factor for plutonium.

$t_w(x)$ = The time required for the groundwater to travel from the system origin ($x=0$) to a point x .

In order to make this calculation and others more physically meaningful for the case of Yucca Mountain (with an accessible environment boundary at 5,000 m from the repository), it is further assumed that:

- (i) The repository inventory of $^{239}\text{Pu} = 2.1 \times 10^7$ Ci (15, assuming a repository capacity of 70,000 metric tons of uranium)
- (ii) The rate of water flow through the repository is uniform and equals 9.43×10^4 L/yr, (3)
- (iii) The solubility of plutonium equals 10^{-10} moles/L^a and that the water flowing through the repository becomes saturated and is not diluted along its path to the accessible environment
- (iv) $R_y^{\text{Pu}} = 251$ (using data from 4)
- (v) $t_w(x = 5,000 \text{ m}) = 1,000 \text{ yr}$
- (vi) $\lambda_2^P = 2.89 \times 10^{-5} \text{ yr}^{-1}$

Assuming that the groundwater becomes saturated with plutonium as it passes the waste packages, one calculates that the concentration of plutonium in the groundwater at $x=0$ is:

$$c_{2,0} = 6.0 \times 10^{13} \left(\frac{\#}{l} \right) \quad (9)$$

Substituting Equation (9) into Equation (8) and using the values for R_y^{Pu} , t_w , and λ_2^P listed previously yields a solution for the concentration of plutonium in the groundwater of:

$$c_2(x) = [6.0 \times 10^{13}] \cdot \exp(-0.00145x) \left(\frac{\#}{l} \right) \quad (10)$$

where x is in meters.

The calculated plutonium groundwater concentration profile is plotted in Figure 2.

GROUNDWATER PLUTONIUM CONCENTRATIONS AS CALCULATED USING THE PROPOSED MODEL

Using the assumptions listed in the beginning of this section along with the improved sorption model described earlier, the differential equations describing the groundwater concentrations of both uranium (radionuclide 1) and plutonium (radionuclide 2) are respectively:

$$\frac{\lambda_1^P}{\epsilon} \left\{ \frac{\rho_b K_d^1 c_1(x)}{1 + \frac{1}{n_T} [\rho_b K_d^1 c_1(x) + \rho_b K_d^2 c_2(x)]} \right\} = \lambda_1^P c_1(x) + U_0 \frac{d}{dx} c_1(x) \quad (11)$$

$$\frac{\lambda_2^P}{\epsilon} \left[\frac{\rho_b K_d^2 c_2(x)}{1 + \frac{1}{n_T} [\rho_b K_d^2 c_2(x) + \rho_b K_d^1 c_1(x)]} \right] = \lambda_2^P c_2(x) + U_0 \frac{d}{dx} c_2(x) \quad (12)$$

The groundwater plutonium concentration profile can be found by simultaneously solving Equations (11) and (12). To make the system solvable analytically, it is assumed that:

$$(i) \quad K_d^1 c_1(x) > K_d^2 c_2(x)$$

$$(ii) \quad \frac{\rho_b K_d^1}{n_T} c_1(x) > 1$$

It is further assumed that there is negligible radioactive decay of uranium in transport. The

justification for this assumption is that the half-life of ^{238}U is sufficiently long (4.5×10^9 yr) when compared to an estimate of the maximum radionuclide travel time through the media of $R_f^* t_w$ (26,000 yr). This assumption leads to a solution of Equation (11) for $c_1(x)$ of:

$$c_1(x) = c_{1,0} \quad (13)$$

This procedure yields a solution for $c_2(x)$ of:

$$c_2(x) = c_{2,0} \exp \left[- \frac{\lambda_2^P}{U_0} \left(1 + \frac{1}{\epsilon} \frac{K_d^2}{K_d^1} \frac{n_T}{c_{1,0}} \right) x \right] \quad (14)$$

The parameters and data for plutonium used in the previous section are used again in this section along with the following assumptions:

- (i) The repository inventory of ^{238}U equals 2.1×10^4 Ci (15)
- (ii) The solubility of uranium equals 2×10^{-5} moles/L^b and that the water flowing through the repository becomes saturated and is not diluted along its path to the accessible environment
- (iii) $R_f^U = 26$ [using data from 4, but adjusted upward based on data from the Center for Nuclear Waste Regulatory Analyses (CNWRA)]^c

Assuming that the groundwater is saturated with uranium as it passes the waste packages, one finds:

$$c_{1,0} = 1.2 \times 10^{19} \left(\frac{\#}{l} \right) \quad (15)$$

In order to complete this procedure, values for n_T must be known. This investigator was unable to

find any realistic data for n_T for rock typical of Yucca Mountain; therefore, n_T will be treated as a parameter in the rest of the analysis.

Substituting the appropriate parameter values into Equation (14) one finds:

$$c_2(x) = [6.0 \times 10^{13}] \cdot \exp[-(5.77 \times 10^{-6}) \cdot (1 + 8.47 \times 10^{-18} n_T)x] \quad (16)$$

Figure 2 shows the groundwater plutonium and uranium concentration profiles as calculated by the constant retardation factor model and the new model with n_T as a parameter. The range of values for n_T was chosen because its range is several orders of magnitude less than that of Environmental Protection Agency activated carbon (6). This range was chosen because activated carbon is quite fractured and granulated by nature and, thus, should contain significantly more adsorber sites than rock typical of Yucca Mountain. Also, this data range seems to agree with ranges from (14).

One can easily see from Figure 2 that accounting for the competitive nature of radionuclide sorption can have significant impact on predictions of groundwater plutonium concentrations. Specifically, the constant retardation factor model predicts groundwater plutonium concentrations that are about 3 orders of magnitude less conservative than the new model. The difference between the two models would become even more pronounced as more radionuclides are added to the system since plutonium ions would be competing for adsorber sites with those other radionuclides as well. The assumptions used in this section were not made because they are a necessity of the model, but were made to make the example transparent to the reader. In general, Equations (1) through (5) would be solved numerically to find groundwater radionuclide species concentrations. In reality, plutonium will not only be competing with itself and uranium for sorber sites, but will also be competing with many other radionuclide species and naturally occurring ions. This fact leads to a conclusion that the spread between the two model predictions will, in general, be even larger.

CONCLUSIONS

This paper describes an improved model to account for the effects of sorption of radionuclides on rock surfaces during liquid phase transport of radionuclides away from a HLW geologic repository. The model presented here does not have the difficulties that the retardation factor model, currently used in Yucca Mountain PA work, has in that it is capable of accounting for the competitive nature of radionuclide sorption and the reduction of the sorption capabilities of geologic media due to occupation of sorption sites by other nuclides. The model presented in this paper should work well provided that the monolayer adsorption approximation is valid. Data presented in (14), as fit by that paper's author's diffuse layer surface complexation model, would suggest that this approximation is valid for the general case.

Using the derived model versus a simple constant retardation factor approach can have significant impact on calculations of groundwater radionuclide concentrations. At 5,000 m there was approximately a three order of magnitude difference between groundwater ^{239}Pu concentration calculations using the two different models for a simple system composed of ^{238}U , ^{239}Pu , water, and rock properties typical of Yucca Mountain, with the constant retardation factor model being less conservative. Essentially what was seen in this case was that ^{238}U was able to block enough of the sorber sites such that ^{239}Pu was able to pass through unimpeded by sorption. The mathematical simplifications made during these calculations were done to make the calculations transparent to the reader. Although these simplifications are realistic in the context presented, in general the differential equations would be numerically solved using site characterization data or stochastic methods to incorporate this sorption model into existing PA methodology.

It is envisioned that the model presented in this paper can be directly coupled to models that predict the flow velocity of groundwater in geologic media. This is due to how the groundwater spatial velocity term and the sorption site density directly couple into the sorption equations, meaning that the model could be incorporated into existing PA models provided that sufficient data exist.

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QUALITY OF DATA, ANALYSES, AND CODE DEVELOPMENT

DATA: CNWRA-generated data contained in this report meets quality assurance requirements described in the CNWRA Quality Assurance Manual. Sources for other data should be consulted for determining the level of quality for those data.

ANALYSES AND CODES: No computer codes were used in this report.

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APPENDIX A

In order to extract the data that the improved sorption model needs from existing data (namely K_d s), a one species, spatially homogenous, saturated system where the species does not radioactively decay in steady-state is considered where it is assumed, for simplicity, that the media exhibits only the adsorption property for the radionuclide. Under these circumstances, Equations (4) and (5) both become:

$$c = \frac{\lambda^c \kappa}{(k^0)' \left[1 - \frac{n}{n_T} \right]} \quad (\text{A-1})$$

Since there are two unknowns and only one equation, another equation must be derived to completely describe the system. Consider an introduction of s_0 atoms per unit volume of the radionuclide being investigated, then:

$$c = s_0 - n \quad (\text{A-2})$$

Recall that the distribution coefficient is defined as the ratio of the number of atoms in the sorbed state per gram of sorption media to the number of atoms in solution per milliliter of solution. Or, in terms of the parameters listed above:

$$K_d = \frac{n}{\rho_b c} \quad (\text{A-3})$$

where ρ_b equals the bulk density of the sorbing media.

Using these assumptions leads to an expression for the distribution coefficient:

$$K_d = \frac{n}{\rho_b C} = \frac{\left[\frac{\lambda^C}{(k^0)'} + \frac{s_0}{n_T} + 1 \right] - \sqrt{1 + 2 \left[\frac{\lambda^C}{(k^0)'} - \frac{s_0}{n_T} \right] + \left[\frac{\lambda^C}{(k^0)'} + \frac{s_0}{n_T} \right]^2}}{\rho_b \left\{ \left[-\frac{\lambda^C}{(k^0)'} + \frac{s_0}{n_T} - 1 \right] + \sqrt{1 + 2 \left[\frac{\lambda^C}{(k^0)'} - \frac{s_0}{n_T} \right] + \left[\frac{\lambda^C}{(k^0)'} + \frac{s_0}{n_T} \right]^2} \right\}} \quad (\text{A-4})$$

One should note that Equation (A-4) has the expected form with respect to increasing s_0 , (at small values of s_0 , K_d is approximately constant and at exceedingly large values of s_0 , K_d approaches zero).

In the low atomic concentration limit, Equation (A-4) becomes:

$$K_d = \frac{1}{\rho_b} \frac{(k^0)'}{\lambda^C} \quad (\text{A-5})$$

As an example, consider the cases of plutonium and uranium that are used throughout this paper. Using the median K_d value for plutonium from (4) for devitrified tuff (K_d for plutonium = 125 cm³/g), and a K_d value for uranium that is the median value from (4) but adjusted upward based on data from the CNWRA (K_d for uranium = 12.5 cm³/g), substituting these values into Equation (A-5) (assuming that the K_d values from that report actually denote the low atomic concentration ($s_0 \rightarrow 0$) distribution coefficients), and using a bulk density for the rock of 2 g/cm³, one finds:

$$\frac{(k_1^0)'}{\lambda_1} \approx \frac{(k_1^0)'}{\lambda_1^C} = 300 \quad (\text{A-6})$$

$$\frac{(k_2^0)'}{\lambda_2} \approx \frac{(k_2^0)'}{\lambda_2^C} = 250 \quad (\text{A-7})$$

where it has been assumed that radioactive decay is negligible when compared with chemical

desorption. It is envisioned that the same methodology could be used to extract parameter values for other radionuclides as well.

APPENDIX B

NOMENCLATURE

- $c_i(\bar{r}, t)$ The groundwater concentration of radionuclide species i .
- $n_i^c(\bar{r}, t)$ The number of atoms of radionuclide species i that are adsorbed to rock surfaces and remain covered with water, per unit total volume (volume of rock plus pores).
- $n_i^u(\bar{r}, t)$ The number of atoms of radionuclide species i that are adsorbed to rock surfaces and then have become uncovered with water per unit total volume.
- $q_i^c(\bar{r}, t)$ The number of radionuclide species i that are bound to the rock surfaces through an ionic bond and remain covered with water per unit total volume.
- $q_i^u(\bar{r}, t)$ The number of radionuclide species i that are bound to the rock surfaces through an ionic bond and have become uncovered with water.
- $n_T(\bar{r})$ The number of adsorber sites per unit total volume.
- λ_i^C The desorption (de-adsorption) or "chemical decay" coefficient for radionuclide species i , (chemical decay refers to the fact that the radionuclide is changing its chemical state (free versus adsorbed) and not its physical state, as is the case with radioactive decay).
- λ_i^P The radioactive or physical decay constant for radionuclide species i .
- λ_i $\lambda_i^P + \lambda_i^C$.
- $\lambda_{j \rightarrow i}^P$ The radioactive or physical decay constant for radionuclide species j that results in the production of radionuclide species i .

- $k_{j \rightarrow i}^E$ The ion-exchange rate constant for radionuclide species j substituting for radionuclide species i .
- $(k_i^0)'$ The number of atoms of radionuclide species i adsorbed per unit total volume per unit time per unit concentration of radionuclide species i in the groundwater, in the absence of any adsorbed atoms on the rock surfaces.
- K_d^i The distribution coefficient for radionuclide species i .
- R_f^i The retardation factor for radionuclide species i .
- v_i The valence of radionuclide species i .
- ϵ The rock porosity equals the volume of pore space per unit total volume.
- $s(\vec{r}, t)$ The saturation fraction equals the fraction of the pore space that is filled with water. This approximates, to first order, the fraction of adsorber sites that are exposed to groundwater.
- $R_{i \rightarrow k}$ The reaction rate (per unit concentration) of radionuclide species i with other groundwater constituents that results in the production of radionuclide species k .
- $\vec{U}(\vec{r}, t)$ The pore velocity of the interstitial fluid (water) as a function of position and time.
- $D_i(\vec{r}, t)$ The diffusion coefficient of radionuclide species i in the media as a function of position and time = $f[\epsilon, \tau, s(\vec{r}, t)] \cdot D_{wi}$, where:
- $f[\epsilon, \tau, s(\vec{r}, t)]$ = A function of the listed parameters
- τ = The tortuosity of the media
- D_{wi} = The diffusion coefficient of radionuclide species i in water

FIGURE CAPTIONS

- Figure 1 A view of the differential volume
- Figure 2 A plot of the groundwater uranium and plutonium concentration versus distance
into the media as calculated by the different models

FOOTNOTES

- a Personal conversation with R. Codell.
- b Personal conversation with R.T. Pabalan.
- c Personal conversation with R.T. Pabalan.

AN IMPROVED METHOD FOR MODELLING SOLUTION OF RADIONUCLIDES DURING LIQUID PHASE TRANSPORT FOR PERFORMANCE ASSESSMENTS OF HIGH-LEVEL WASTE REPOSITORIES - M.S. JARZEMBA, FIGURE 1



