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DISCLAIMER

Near-Field Transport of Radioactive Chains

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NEAR-FIELD TRANSPORT OF RADIOACTIVE CHAINS

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ABSTRACT

Much attention has been given to predicting the near-field mass transfer of a single radioactive species from a waste solid into surrounding porous material, but only limited consideration has been given to predicting the coupled mass transfer of species in a radioactive decay chain. Here we present an analysis that assumes that the members of a decay chain dissolve congruently with a solubility-limited matrix. Here "dissolution" refers to the net process of dissolving in ground water. A solid species that may temporarily dissolve in interacting with water to form a precipitate is not considered to have dissolved. We give the general, non-recursive analytic solutions for the transport of a radioactive decay chain in a finite porous medium when nuclides are released congruently with the matrix. To illustrate we consider the decay chain $^{234}U \rightarrow ^{230}Th \rightarrow ^{226}Ra$ from spent fuel. These solutions are useful and potentially important in performance assessment of nuclear waste repositories.

INTRODUCTION

In nuclear waste and mixed waste studies, much attention has been given to predicting the transport of a single radioactive species from the waste into surrounding porous material, but only limited consideration has been given to predicting the coupled transport of species in a radioactive decay chain. Failure to account for nuclides generated during transport may underestimate releases to the biosphere. In this paper we present some general analytic solutions for the transport of radioactive chains of arbitrary length, in finite porous media, for congruent release at the source. The analytic solutions have been coded into efficient computer codes. We present illustrations of the transport of chains from high-level nuclear waste, calculated using these computer codes.

BACKGROUND

Many solutions and computer codes for the transport of radioactive chains exist. Most of them have limitations. Some use approximations. Some are limited by the number of chain members. Others give a recursive solution. Harada et al.[1] developed the equations for transport of a radioactive decay chain assuming a constant mass rate of dissolution of waste solid. Chambré et al.[2] obtained the general, non-recursive analytic solution for the transport of radioactive chains of arbitrary length. Lung et al.[3] implemented the general solution in finite and semi-infinite porous media for time-dependent mass transfer assuming that each member of the decay chain is at a specified constant concentration at the waste surface and for band release at the waste surface. These solutions are useful for many situations in radioactive and mixed wastes where a constant concentration, such as the solubility, can be specified. However, for radioactive species dissolving from a solid waste form, as in high-level nuclear waste or spent nuclear fuel, a more sophisticated analysis is needed. Kang[4] solved the equations, assuming, more realistically, that the members of a decay chain dissolve congruently with a solubility-limited matrix.

CONGRUENT DISSOLUTION

In this paper "dissolution" refers to the net process of dissolving in ground water. A solid species that may temporarily dissolve in interacting with water to form a precipitate is not considered here to have dissolved. However, the precipitate may undergo dissolution and mass transport into the surrounding porous media.

Congruent dissolution of two species means that the ratio of the time-dependent mass rates of dissolution of those species equals the ratio of the time-dependent concentrations of those species in the dissolving solid.[5] Congruent dissolution is expected if there is no preferential leaching of any constituent in the waste solid. For example,

in a reducing environment the UO_2 matrix of spent fuel appears to dissolve congruently with the soluble constituents of spent fuel. However, if any constituent is of sufficiently low solubility, that species may not be able to all dissolve as it is released from the solid matrix by uranium dissolution. The dissolution of that low-solubility species is not congruent with the dissolution of the uranium, although the release of that species and uranium from the UO_2 matrix solid may be congruent. The released low-solubility species can form a precipitate at the waste surface. If that species has no radioactive-decay precursors, its dissolution rate can be predicted from the mass-transfer equations for a solubility-controlled single species. In our analysis, we assume that the first member of a chain is dissolved congruent with the waste matrix, and that daughters of the chain are released congruent to the first member.

Our assumption that radioactive-decay daughters dissolve congruently with the first member of the decay chain can be justified for the decay chain

$$^{234}U \rightarrow {}^{230}Th- \; {}^{226}Ra$$
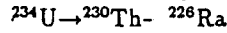
usually the most important decay chain to consider in performance assessment of nuclear waste repositories.

GENERAL SOLUTION

Consider the canonical system for $z \in \mathcal{D}, t > 0$

$$K_1 \frac{\partial c_1}{\partial t} + v \frac{\partial c_1}{\partial z} + \lambda_1 K_1 c_1 = D_1 \frac{\partial^2 c_1}{\partial z^2}$$

$$K_2 \frac{\partial c_2}{\partial t} + v \frac{\partial c_2}{\partial z} + \lambda_2 K_2 c_2 = D_2 \frac{\partial^2 c_2}{\partial z^2} + \lambda_1 K_1 c_1$$

$$\vdots \qquad \vdots \qquad \vdots$$

$$K_i \frac{\partial c_i}{\partial t} + v \frac{\partial c_i}{\partial z} + \lambda_i K_i c_i = D_i \frac{\partial^2 c_i}{\partial z^2} + \lambda_{i-1} K_{i-1} c_{i-1} \quad (1)$$

where
$c_i(z,t)$ is the concentration of the ith member, $[M/L^3]$
D_i is the species dispersion coefficient, $[L^2/t]$
K_i is the species retardation coefficient, and
λ_i the species decay constant, $[t^{-1}]$.
Eq. (1) is subject to the initial condition

$$c_i(z,0) = 0, \qquad z > 0 \qquad (2)$$

and the boundary condition

$$-D_i \epsilon \frac{\partial c_i}{\partial z} + v c_i = v c_i^0 \phi_i(t),$$

$$for \; z = 0, \quad t > 0 \; and \; \phi_i(t) \equiv 0 \; for \; t < 0 \qquad (3)$$

The left-hand side of the boundary condition states the local flux of species i through the boundary surface at

z of $\mathcal{D}$ while the right-hand side describes the rate of supply of the species in terms of the arbitrarily prescribed integrable function $c_i^0 \phi_i(t)$. These functions describe the time release of the chain members from the waste located at $z = 0$. ϵ is the porosity of the medium. In case of negligible advection the terms involving v vanish from (1). The boundary condition at the outer boundary of $\mathcal{D}$ will be stated later.

The general form of the equation system (1) is

$$\frac{K_i}{D_i} \frac{\partial c_i}{\partial t} + \frac{v}{D_i} \frac{\partial c_i}{\partial z} + \nu_i c_i = \frac{\partial^2 c_i}{\partial z^2} + \nu_{i-1} c_{i-1},$$

$$z > 0, \quad t > 0, i = 1, 2, \ldots \quad (4)$$

where

$$\nu_i = \frac{K_i \lambda_i}{D_i}, \qquad \nu_{i-1} = \frac{K_{i-1} \lambda_{i-1}}{D_1}$$

The aim is to obtain the general (non-recursive) analytic solution for $c_i(z,t)$. Because of the linear nature of (4), the general analytic solution for $c_i(z,t)$ can be expressed as a sum of functions. For example, for the ith member of any chain

$$c_i(z,t) = c_i^{(i)}(z,t) + \sum_{j=1}^{i-1} c_i^{(j)}(z,t), z > 0, t > 0, i = 1, 2, \ldots \quad (5)$$

If this decomposition is used, then the equation system (1) - (4) can be written as

$$\frac{K_\ell}{D_\ell} \frac{\partial c_\ell^{(j)}}{\partial t} + \frac{v}{D_\ell} \frac{\partial c_\ell^{(j)}}{\partial z} + \nu_\ell c_\ell^{(j)} = \frac{\partial^2 c_\ell^{(j)}}{\partial z^2} + \nu_{\ell-1} c_{\ell-1},$$

$$0 < z < \infty, t > 0, \nu_o = 0, \ell = 1, 2, \ldots i, j \leq \ell \quad (6)$$

$$c_\ell^{(j)}(z,0) = 0, \qquad z > 0 \qquad (7)$$

$$-D_\ell \epsilon \frac{\partial c_\ell^{(j)}(0,t)}{\partial z} + v \epsilon c_\ell^{(j)}(0,t) = \delta_{\ell j} v \epsilon c_j^0 \phi_j(t), \quad j \leq \ell, t > 0 \quad (8)$$

where $\delta_{\ell j}$ is the Kronecker delta that vanishes for $\ell \neq j$ and is unity for $\ell = j$.

Furthermore

$$c_{\ell-1}^{(j)}(z,t) \equiv 0, \; for \; \ell \leq j \qquad (9)$$

which assures that for $\ell \leq j$ the inhomogeneous source term $\nu_{\ell-1} c_{\ell-1}$ vanishes.

Take the Laplace transform of (6) with respect to the time variable and define

$$\bar{c}_\ell^{(j)}(z,s) \equiv \int_0^\infty e^{-st} c_\ell^{(j)}(z,t) dt, \quad \bar{\phi}_j(s) \equiv \int_0^\infty \phi_j(t) dt$$

$$(10)$$

The transform of (6), on using the initial condition (7), yields

$$\frac{d^2\bar{c}_\ell^{(j)}}{dz^2} - \frac{v}{D_\ell}\frac{d\bar{c}_\ell^{(j)}}{dz} - \left(\frac{K_\ell}{D_\ell} + \nu_\ell\right)\bar{c}_\ell^{(j)} = -\nu_{\ell-1}\bar{c}_{\ell-1}^{(j)} \quad (11)$$

for $\bar{c}_\ell^{(j)}(z,s)$. The first-order derivative term can be removed by the transformation

$$\bar{c}_\ell^{(j)}(z,s) = e^{vz/2D_\ell}n_\ell^{(j)}(z,s) \quad (12)$$

Then

$$\frac{d^2 n_\ell^{(j)}}{dz^2} - \left[\frac{K_\ell}{D_\ell} + \nu_\ell + \left(\frac{v}{2D_\ell}\right)^2\right]n_\ell^{(j)} =$$

$$-\nu_{\ell-1}n_{\ell-1}^{(j)}\exp\left\{-\frac{vz}{2}\left(\frac{1}{D_\ell} - \frac{1}{D_{\ell-1}}\right)\right\} \quad (13)$$

Introducing these variables,

$$\mu_\ell \equiv \left(\frac{K_\ell}{D_\ell} + a_\ell\right), \quad a_\ell \equiv \left[\nu_\ell + \left(\frac{v}{2D_\ell}\right)^2\right] \quad (14A)$$

$$\gamma_\ell \equiv \frac{v}{2}\left(\frac{1}{D_\ell} - \frac{1}{D_{\ell-1}}\right) \quad (14B)$$

we can simplify (13) into compact form

$$\frac{d^2 n_\ell^{(j)}(z,s)}{dz^2} - \mu_\ell n_\ell^{(j)}(z,s) = -\nu_{\ell-1}n_{\ell-1}^{(j)}(z,s)e^{-\gamma_\ell z}, \quad j \leq \ell \quad (15)$$

which is the fundamental governing equation that we will solve for various boundary conditions. The details of the general solution are given by Chambré et al..[2]

We now make a simplifying assumption. There is little experimental data on the diffusion/dispersion coefficients of chain members. Therefore we shall assume

$$D_\ell = D, \quad for\ all\ \ell \quad (16)$$

Then γ_ℓ vanishes, and (15) simplifies to

$$\frac{d^2 n_\ell^{(j)}(z,s)}{dz^2} - \mu_\ell n_\ell^{(j)}(z,s) = -\nu_{\ell-1}n_{\ell-1}^{(j)}(z,s), \quad j \leq \ell \quad (17)$$

The boundary condition (8) transforms to

$$-D\epsilon\frac{\partial n_\ell^{(j)}(0,s)}{\partial z} + \frac{\epsilon v}{2}n_\ell^{(j)}(0,s) = \delta_{\ell j}c_\ell^o v\epsilon\phi_\ell(s), \quad j \leq \ell \quad (18)$$

THE GENERAL SOLUTION IN FINITE DOMAIN

To obtain the general solution in a finite porous medium, we need to specify a boundary condition at the outer boundary of $\mathcal{D}$. In the finite domain $\mathcal{D}_f, 0 \leq z \leq L$, where L is the width of the span, we specify a Type-III boundary condition

$$-D_i\epsilon\frac{\partial c_i}{\partial z} + v\epsilon c_i = h\left[c_i - c_i^q(t)\right], \quad for\ z = L, \quad t > 0 \quad (19)$$

where c_i^q is the average concentration of the nuclide outside of the region and h is an assumed constant mass-transfer coefficient describing the mass flux at $z = L$. Upon the application of the Laplace transform and (12) to (19) we obtain the transformed boundary condition

$$D_\ell\frac{\partial n_\ell^{(j)}(L,s)}{\partial z} + \left[h - \frac{\epsilon v}{2}\right]n_\ell^{(j)}(L,s) = \delta_{\ell j}he^{vL/2D}c_\ell^q(s), j \leq \ell \quad (20)$$

Our problem is to solve the governing equation (17), with the initial condition (7), and boundary conditions (18) and (20). As shown in Chambré et al.,[2] a Fourier transform is taken of (17) with respect to the variable z. Upon inversions of the Laplace transform and the Fourier transform, the result is the general, non-recursive solution in $\mathcal{D}_f$ with the $\star$ symbol denoting the convolution integral,

$$c_i(z,t) = \exp\left\{\frac{vz}{2D}\right\}\frac{D}{K_i}\left\{\sum_{m=1}^{\infty}\mathcal{K}(\beta_\ell,z)g_i(\beta_\ell,t) \star e^{-\delta_i t}dp\right.$$

$$\left. + \sum_{j=1}^{i-1}C_i^{(j)}\sum_{n=j}^{i}\sum_{\ell=1}^{\infty}\frac{\mathcal{K}(\beta_\ell,z)g_i(\beta_\ell,t) \star e^{-\delta_n t}}{\prod_{\substack{r=j \\ r\neq n}}^{i}(\Gamma_{nr}\beta_\ell^2 + \gamma_{nr})}\right\},$$

$$z > 0, t > 0, i = 1,2,\ldots \quad (21)$$

where $\mathcal{K}$ the kernel

$$\mathcal{K}(\beta_\ell,z) = \sqrt{2}\frac{\beta_\ell \cos(\beta_\ell z) + \alpha_1 \sin(\beta_\ell z)}{\left[(\beta_\ell^2 + \alpha_1^2)\left(L + \frac{\alpha_2}{\beta_\ell^2 + \alpha_2^2}\right) + \alpha_1\right]^{1/2}} \quad (22)$$

and the eigenvalues, β_ℓ, form a discrete, countable spectrum. The β_ℓ's are given by the solutions of the transcendental equations

$$\tan(\beta_\ell, L) = \frac{\beta_\ell(\alpha_1 + \alpha_2)}{\beta_\ell^2 - \alpha_1\alpha_2}, \quad \ell = 1,2,\ldots \quad (23A)$$

$$g_\ell(\beta_\ell,s) \equiv \frac{\mathcal{K}(\beta_\ell,L)}{D\epsilon}he^{vL/2D}c_\ell^q + \frac{\mathcal{K}(\beta_\ell,0)}{D\epsilon}c_\ell^o v\epsilon\phi_\ell(s), \quad (23B)$$

3

$$\alpha_1 = \frac{v}{2D} \qquad \alpha_2 = \frac{h - v\epsilon/2}{D\epsilon} \qquad \delta_n = \frac{D}{K_n}(\beta_\ell^2 + a_\ell) \qquad \ell = 1, 2, \dots$$

$$(23C)$$

CONGRUENT DISSOLUTION AT INNER BOUNDARY

Here we consider a matrix species whose dissolution is controlled by matrix solubility, and we assume other species dissolve congruently with the matrix. In light of the introduction, the "matrix" for this purpose could be uranium dioxide in spent nuclear fuel in a reducing environment, or it could be the precipitate of ^{238}U, ^{234}U, and other uranium isotopes that will form on the surface of spent fuel in an oxidizing environment or on glass waste.

In this case we have to deal separately with the matrix species and the chain members. If the matrix dissolution is controlled by matrix solubility, then the foregoing analysis is directly applicable.

The governing equation for the matrix species is

$$K_m \frac{\partial c_m}{\partial t} + v \frac{\partial c_m}{\partial z} + \lambda_m K_m c_m = D_m \frac{\partial^2 c_m}{\partial z^2}, \qquad z > 0, \ t > 0$$

$$(24)$$

which is to be solved for the concentration of the matrix species, $c_m = c_m(z,t)$. Here subscript m is for the matrix species, D is the dispersion coefficient, K_m the retardation coefficient, λ_m the decay constant, and v the ground-water pore velocity. With the initial condition

$$c_m(z,0) = 0, \qquad z \in \mathcal{D}_\infty \qquad (25)$$

and the boundary conditions

$$c_m(0,t) = c_s, \qquad t \geq 0 \qquad (26)$$

where c_s is the solubility of the matrix species.

The governing equation for the members of the decay chain is (1). Initial condition (2) applies. We shall write the boundary condition for the chain members at the inner surface as

$$-D_i \epsilon \frac{\partial c_i}{\partial z} + v\epsilon c_i = \dot{M}_i(t), \quad for \ z = 0, t > 0 \qquad (27)$$

where $\dot{M}_i(t)$ is the mass transfer rate of species i from the waste into the finite span.

$\dot{M}_i(t)$ is determined from the definition of congruent release

$$\frac{\dot{M}_m(t)}{M_m(t)} = \frac{\dot{M}_i(t)}{M_i(t)}, \qquad t \geq 0 \qquad (28)$$

or

$$\dot{M}_i(t) = \dot{M}_m(t) \frac{M_i(t)}{M_m(t)}, \qquad t \geq 0 \qquad (29)$$

where $M_m(t)$ and $\dot{M}_m(t)$ are the inventory and the mass flux of the matrix species, respectively, and $M_i(t)$ and $\dot{M}_i(t)$ are those of the ith member.

To solve this system we proceed as follows.

1. Solve the governing equation with side conditions and compute the mass flux of the matrix species, $\dot{M}_m(t)$ at the waste/rock interface, $z = 0$

2. From equation (29), compute $\dot{M}_i(t)$ at $z = 0$

3. Solve the governing equation with appropriate side conditions for the individual chain members.

The boundary condition at $z = L$ for the matrix is

$$-D_m \epsilon \frac{\partial c_m}{\partial z} + v\epsilon c_m = h c_m \qquad for \ z = L, \ t > 0 \quad (30)$$

where h is the mass-transfer coefficient for the outer medium, assumed to be constant at the steady-state value.

The boundary condition at $z = L$ for the ith member is

$$-D_i \epsilon \frac{\partial c_i}{\partial z} + v\epsilon c_i = h c_i \qquad for \ z = L, \ t > 0$$

$$(31)$$

We apply the general solution (21) to the matrix and the solution for the matrix species is

$$c_m(z,t) = \exp\left\{\frac{vz}{2D}\right\} \frac{D}{K_i} c_s$$

$$\times \sum_{\ell=1}^{\infty} \left[\frac{2}{L + \varsigma_\ell}\right] \frac{\beta_\ell \sin \beta_\ell z}{\delta_m} \left(1 - e^{-\delta_m t}\right) \qquad (32)$$

We first compute the boundary concentration, $c_i(0,t)$

$$c_i(0,t) = \frac{D}{K_i} \left\{ \sum_{\ell=1}^{\infty} \mathcal{K}(\beta_\ell, z) g_i(\beta_\ell, t) * e^{-\delta_i t} \right.$$

$$\left. + \sum_{j=1}^{i-1} C_i^{(j)} \sum_{n=j}^{i} \sum_{\ell=1}^{\infty} \frac{\mathcal{K}(\beta_\ell, z) g_i(\beta_\ell, t) * e^{-\delta_n t}}{\prod_{\substack{r=j \\ r \neq n}}^{i} (\Gamma_{nr} \beta_\ell^2 + \gamma_{nr})} \right\}$$

$$= \frac{2c_s}{M_m^0 K_i} \left\{ \sum_{k=1}^{i} B_{ik} \sum_{\ell=1}^{\infty} \frac{\beta_\ell^2}{(\beta_\ell^2 + \alpha_2^2)\left[L + \frac{\alpha_2}{\beta_\ell^2 + \alpha_2^2}\right] + \alpha_1} \text{conv}(p; k, i) dp \right.$$

$$\left. + \sum_{j=1}^{i-1} C_i^{(j)} \sum_{n=j}^{i} \sum_{\ell=1}^{\infty} \left\{ \frac{1}{\prod_{\substack{r=j \\ r \neq n}}^{i} (\Gamma_{nr} \beta_\ell^2 + \gamma_{nr})} \right\} \right\}$$

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$$\times \left\{ \frac{\beta_\ell^2}{(\beta_\ell^2 + \alpha_2^2)\left[L + \frac{\alpha_2}{\beta_\ell^2 + \alpha_2^2}\right] + \alpha_1} \right\} conv(p;k,n)dp \right\}, \quad t \geq 0 \tag{33}$$

where

$$conv(p;i,n) =$$

$$= \frac{v}{2} \frac{1}{\lambda_i - \lambda_m - \delta_n} \left(e^{-\delta_n t} - e^{-(\lambda_i - \lambda_m)t} \right) - \frac{D^2}{K_m} \sum_{r=1}^{\infty} \frac{2}{L + \varsigma_r} \frac{\beta_r^2}{\delta_m}$$

$$\times \left\{ \frac{1}{\lambda_i - \lambda_m - \delta_n} \left(e^{-\delta_n t} - e^{-(\lambda_i - \lambda_m)t} \right) \right.$$

$$\left. - \frac{1}{\lambda_i - \lambda_m - \delta_n + \delta_m} \left(e^{-\delta_n t} - e^{-(\lambda_i - \lambda_m + \delta_m)t} \right) \right\}, \quad t \geq 0 \tag{34}$$

Next we solve the system with any arbitrary concentration specified at the boundary, i.e., $c_i(0,t) = f_i(t)$. The solution becomes

$$c_i(z,t) = e^{\frac{vz}{2D}} \frac{D}{K_i} \left\{ \sum_{\ell=1}^{\infty} \left[\frac{2}{L + \varsigma_\ell} \right] \beta_\ell \sin \beta_\ell z f_i(t) * e^{-\delta_i t} \right.$$

$$\left. + \sum_{j=1}^{i-1} C_i^{(j)} \sum_{n=j}^{i} \sum_{\ell=1}^{\infty} \left[\frac{2}{L + \varsigma_\ell} \right] \frac{\beta_\ell \sin \beta_\ell z}{\prod_{\substack{r=j \\ r\neq n}}^{i} (\Gamma_{nr}\beta_\ell^2 + \gamma_{nr})} f_i(t) * e^{-\delta_n t} \right\},$$

$$z > 0, \quad t > 0, \quad i = 1, 2, \dots \tag{35}$$

The flux of the matrix species at the waste surface is

$$\dot{M}_m(t) = \left(-D\epsilon \frac{\partial c_m}{\partial z} + v\epsilon c_m \right) \Big|_{z=0}$$

$$= c_s \epsilon \left(\frac{v}{2} - \frac{D^2}{K_m} \sum_{\ell=1}^{\infty} \frac{2}{L + \varsigma_\ell} \frac{\beta_\ell^2}{\delta_m} \left[1 - e^{-\delta_m t} \right] \right)$$

$$= c_s \epsilon \Psi(t) \tag{36}$$

On substituting (36) into (29) we get

$$\dot{M}_i(t) = c_s \epsilon \Psi(t) \frac{M_i(t)}{M_m(t)}, \quad t \geq 0 \tag{37}$$

Neglecting the mass loss due to the dissolution, the inventories can be written

$$M_m(t) \approx M_m^o e^{-\lambda_m t}, \quad t \geq 0 \tag{38}$$

$$M_i(t) \approx \sum_{j=1}^{i} B_{ij} e^{-\lambda_j t}, \quad t \geq 0 \tag{39}$$

where M_m^o is the initial inventory of the matrix, and B_{ij} the Bateman coefficients

$$B_{ij} = \sum_{k=1}^{j} M_k^o \left(\frac{1}{\lambda_j} \prod_{r=k}^{i} \lambda_r \right) / \prod_{\substack{\ell=k \\ \ell\neq j}}^{i} (\lambda_\ell - \lambda_j) \tag{40}$$

Substitution of (40) into (39), yields the flux of the radionuclide

$$\dot{M}_i(t) = c_s \epsilon \sum_{j=1}^{i} \frac{B_{ij}}{M_m^o} e^{-(\lambda_j - \lambda_m)t} \Psi(t), \quad t \geq 0 \tag{41}$$

Implementation as Computer Codes

Although (21) and (36) are the solutions for this system, they are not a practical form for computing. To overcome computational difficulty, we divide the algorithm into two modules: (1) a module to compute the boundary concentration with congruent release model, and (2) a module to compute the field concentration using the boundary concentration. In the second module we use error functions to replace the integrals, and combine the results with the first exponential term. The detail of the numerical implementation is given separately in the *User's Manual.*[6]

These computer programs are available from the authors and the National Energy Software Center.

Numerical Illustration

We use the $^{234}U \rightarrow ^{230}Th \rightarrow ^{226}Ra$ chain in a spent-fuel matrix of UO_2 to illustrate the solution. This is an important chain in the safety assessment of nuclear waste repositories. The inner layer we consider might consist of backfill around a nuclear waste package, or a damaged rock region. The values used are here for a backfill around a waste package in a wet-rock repository: inner layer thickness $L = 0.30$ m, mass-transfer coefficient $h = 10^{-4}$ m/a, ground-water velocity $v = 0$, diffusion coefficient $D = 10^{-5}$ cm^2/s and porosity of the inner layer $\epsilon = 0.3$.

Table I shows data on the $^{234}U \rightarrow ^{230}Th \rightarrow ^{226}Ra$ chain.

Table I. Data Used in Illustrations

Nuclide	^{238}U	^{234}U	^{230}Th	^{226}Ra
K_i	120	120	1500	300
$T_{1/2}$ (a)	4.5×10^9	2.5×10^5	7.7×10^4	1.6×10^3
M_m^o or M_i^o (g)	1.74×10^6	338	0	0

Figure 1 shows normalized concentration profiles as a function of distance at 10 and 500 years. At 10 years the concentration of ^{230}Th in the field is very low (note that the ordinate is a logarithmic scale). Initially there is no ^{230}Th in the waste and in the field, and all of ^{230}Th comes from the decay of ^{234}U, which has a very long half-life. Therefore one can expect the low concentration of the daughter nuclide in the field at early times as shown in this figure. The concentration of ^{226}Ra is not shown because its value is well below the lower limit (10^{-7}) of this figure. At 500 years ^{234}U has reached steady state, and its value is almost unity in the entire inner layer. The concentrations of ^{230}Th and ^{226}Ra are still rising but the concentration gradient in the inner layer is very small. The surface fluxes are positive as described in the boundary condition.

Figure 2 shows normalized concentrations as a function of time at the interface of the two layers, $z = L$, shown as a solid curve. For comparison, the concentration at the waste surface, $z = 0$, is also shown. The concentration at the layer interface is zero at early time because it takes time for nuclides to diffuse to the interface. At later times the concentration at the interface becomes almost the same as the concentration at the waste surface. This means the concentration in the inner layer has become flat at later times.

Figure 3 shows normalized flux profiles at both ends of the inner layer as a function of time. The solid curves represent the fluxes at the waste surface and the dashed ones represent the fluxes at the layers interface. The trend of the flux at the interface is the same as the trend of the concentration at that point. The mass flux of ^{234}U at $z = 0$ becomes almost equal to that at $z = L$ for $t > 1000$ years. But ^{230}Th does not show this behavior, and the flux at $z = L$ is smaller than that at $z = 0$. The flux of ^{226}Ra at $z = L$ is somewhat higher than that at $z = 0$ at $t > 10^6$ years due to the net birth of ^{226}Ra inside the inner layer.

Figure 4 shows fractional release rates of the nuclides at both ends of the inner layer. The fractional release rates are based on their 1000-year inventories, with the solubility of uranium, $c_s = 10^{-3}$ g/m^3. Because the values in this figure are based on 1000-year inventories, the fractional release rates at 1000 years at the interface are identical for all nuclides, by the definition of congruent release. Because of the continued growth of ^{226}Ra and ^{230}Th in the waste solid, the release rates of these species increase with time. Because of this ingrowth and the 1000-year normalization, the post-1000-year fractional release rates of ^{226}Ra and ^{230}Th are greater than that of ^{234}U. The trends of the fractional release rates into

the outer layer are the same as those into the inner layer except at early times.

CONCLUSIONS

We have given general, non-recursive solutions for the mass transport of a radioactive decay chain in finite porous media when nuclides are released congruently with the matrix species. These analytic solutions have been implemented as modular computer codes.

Numerical illustrations are given for the decay chain ^{234}U$\rightarrow$^{230}Th$\rightarrow$^{226}Ra from spent-fuel waste. To fully analyze the transport of radioactive species, complete consideration of radioactive decay chains is necessary.

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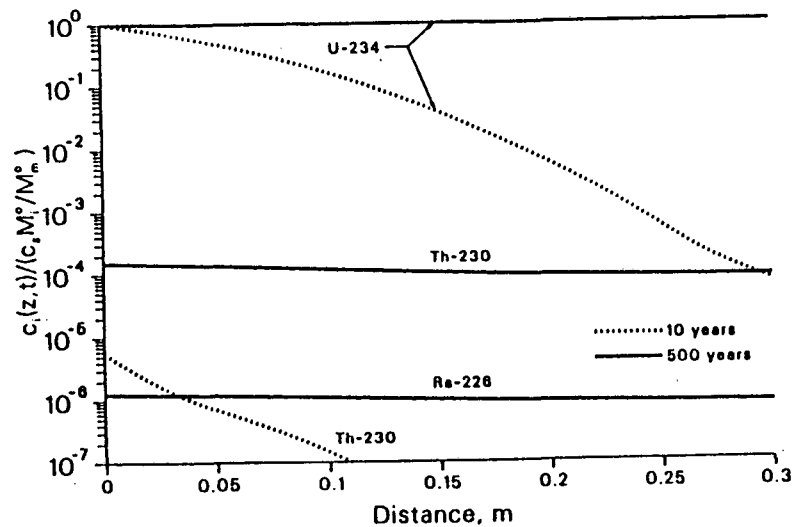6. W. W.-L. LEE and C.-H. KANG. *UCB-NE-130 User's Manual*, Lawrence Berkeley Laboratory (1990).

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Figure 1. Normalized concentration profiles in the finite layer as a function of distance at 10 years and 500 years.
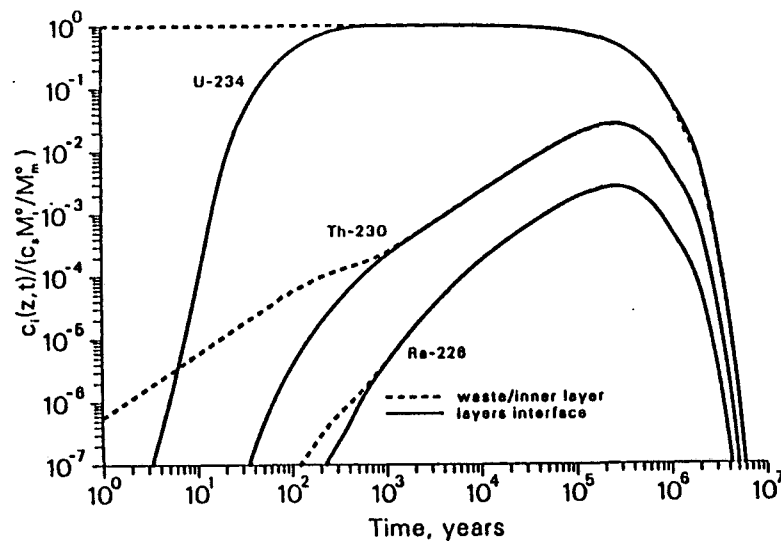

Figure 2. Normalized concentration at both ends of the finite layer as a function of time.
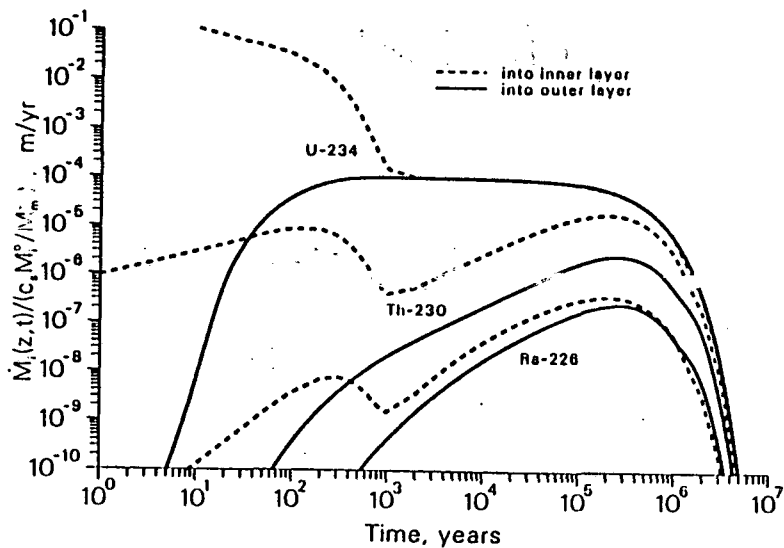

Figure 3. Normalized mass fluxes into and out of the finite layer as a function of time.
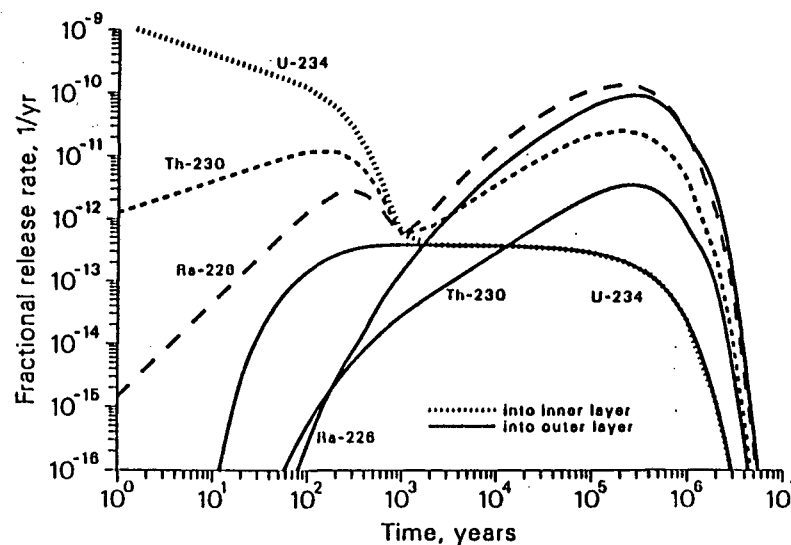

Figure 4. Fractional release rates of radionuclides normalized to their 1000-year inventories as a function of time.

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