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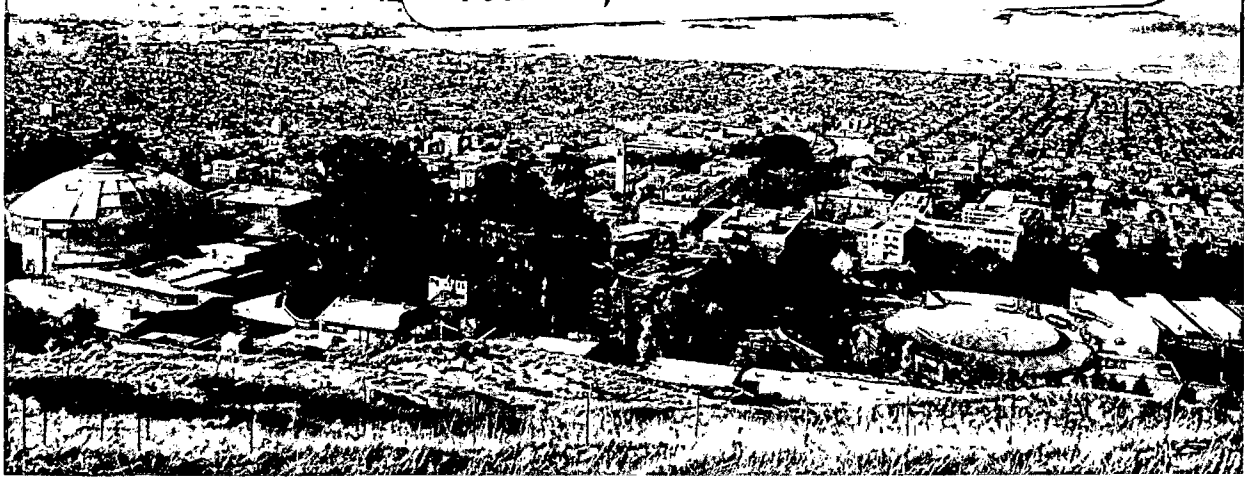

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HYDROGEOLOGIC TRANSPORT WITH EQUILIBRIUM CHEMICAL SPECIES OF RADIONUCLIDES

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TABLE I

Parameters for the Sample Calculations

Chain	^{246}Cm	^{242}Pu	^{238}U	^{234}U	^{230}Th	^{226}Ra
Half-lives (years)	5.5×10^{3}	3.8×10^{5}	4.5×10^{9}	2.5×10^{5}	8.0×10^{4}	1.6×10^{3}
K_i	3.0×10^{3}	1.0×10^{4}	1.4×10^{4}	1.4×10^{4}	5.0×10^{4}	5.0×10^{2}
MPC(Ci/m^3)	4.0×10^{-6}	5.0×10^{-6}	4.0×10^{-5}	3.0×10^{-5}	2.0×10^{-6}	3.0×10^{-8}
M_i (Ci)	1.9	0.2	4.3×10^{-2}	1.2	0.0	0.0

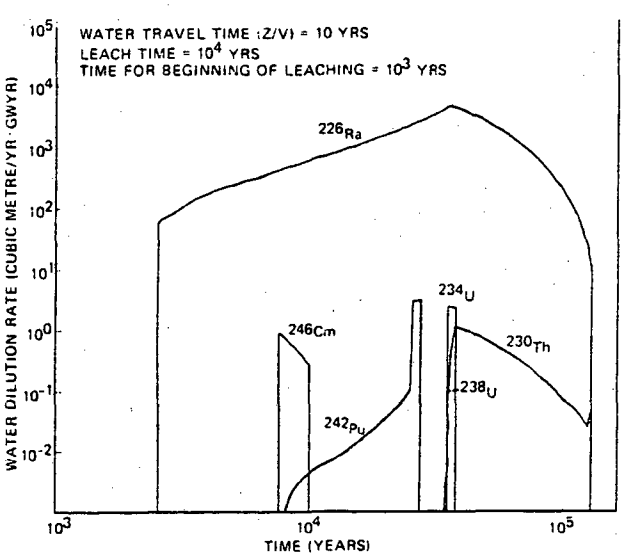

Fig. 1. Sample output of program.

$$g_{rm}(t) = \exp[-\Delta_{rm}(t - K_m\sigma)]\,h(t - K_m\sigma) \quad , \tag{10}$$

$$g_{rm}(t) \circledast \phi_j(t) = \int_0^t g_{rm}(\zeta)\phi_j(t-\zeta)d\zeta \quad . \tag{11}$$

One should note the nonrecursive character of the above solution, which allows one to evaluate the concentration of an arbitrary member of a chain of any length directly, without having to solve for its precursors.

A computer program called MAC-1 (Migration of Actinide Chains) that evaluates the above solution for chains of arbitrary length has been developed. The boundary condition function, Eq. (3), was chosen as a decaying band release with constant leach rate:

$$\phi_i(t) = B_i(t)[h(t) - h(t-T)] \quad .$$

Here, $B_i(t)$ are the Bateman functions, $h(t)$ the step function, and T the duration of the release.

Due to the analytical form of the solution, which does not require recursive calculation, this program presents clear advantages when compared to numerical schemes utilized to solve the partial differential equation system, Eq. (1).

Figure 1 shows a sample output of the program. The concentrations are expressed in terms of the water dilution rate $W_i(z,t)$, which is defined as the volumetric flow rate of the aquifer or surface water into which the migrating radionuclides discharge. So that the concentration of any nuclide should not be above the maximum permissible concentration, $W_i(z,t)$ is given by

$$W_i(z,t) = Q\lambda_i N_i(z,t)/(MPC)_i \quad . \tag{12}$$

The time when the leaching starts is taken as 1000 yr. The chain and its parameters are shown in Table I.

1. M. HARADA et al., "Migration of Radionuclide Through Sorbing Media, Analytical Solutions—I," LBL-10500, Lawrence Berkeley Lab. (1980).

6. Hydrogeologic Transport with Equilibrium Chemical Species of Radionuclides, *T. Kanki (Univ of California, Berkeley), F. Iwamoto (JGC Corp-Japan), P. L. Chambré, T. H. Pigford (Univ of California, Berkeley)*

Many radioelements in radioactive waste can coexist in different oxidation states and/or different chemical compounds, such as NpO_2 and Np^{4}, depending largely on the acidity and oxidation potential of the groundwater. There can be a different value of the sorption retardation constant for each of the chemical species of a given radioelement. Estimates of the migration of radionuclides through a geologic medium must take into account the migration properties of these different species. Hill[1] has illustrated the importance of two different sorbing species of neptunium, assuming no interaction of redistribution between these two species. In the absence of chemical interaction, chromatographic separation of the species can occur. However, the net transport of the radioelement will be quite different if there is a reequilibrium between strongly sorptive and weakly sorptive species. Here we consider an arbitrary number of

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species of a given radionuclide in local chemical equilibrium. We show that the general solution for the hydrogeologic transport of this multispecies system of radionuclides in a decay chain of arbitrary length can be transformed into the general solution for hydrogeologic transport with only a single species for each radionuclide in the decay chain, which we have published elsewhere.[2]

Consider n chemical species of a radioelement and let c_i^m and s_i^m be the space-time-dependent concentrations of species of the nuclide i. In a given phase, the species are assumed to interact according to the system of linear reactions:

$$c_i^1 \ldots c_i^m \underset{k_{fi}^{m+1,m}}{\overset{k_{fi}^{m,m+1}}{\rightleftharpoons}} c_i^{m+1} \ldots c_i^n \ , \quad m = 1,2,\ldots,n \ , \tag{1}$$

$$s_i^1 \ldots s_i^m \underset{k_{si}^{m+1,m}}{\overset{k_{si}^{m,m+1}}{\rightleftharpoons}} s_i^{m+1} \ldots s_i^n \ , \quad m = 1,2,\ldots,n \ . \tag{2}$$

Assuming local chemical equilibrium,

$$c_i^{m+1}/c_i^m = K_{fEi}^m \ , \quad \text{or} \quad c_i^m/c_i^1 = \prod_{j=1}^{m-1} (K_{fEi}^j) \ , \tag{3}$$

$$s_i^{m+1}/s_i^m = K_{sEi}^m \ , \quad \text{or} \quad s_i^m/s_i^1 = \prod_{j=1}^{m-1} (K_{sEi}^j) \ , \tag{4}$$

where $k_{fi}^{m,m+1}$ and $k_{si}^{m,m+1}$ are rate constants for chemical reactions in the water and solid phases, and K_{fEi}^m and K_{sEi}^m are the equilibrium constants in the water and solid phases, respectively. Assuming local sorption equilibrium, namely, $s_i^m/c_i^m = K_{Di}^m$, where K_{Di}^m is the distribution coefficient. The constants K_{fEi}^m, K_{sEi}^m, and K_{Di}^m are related by the equation $K_{sEi}^m/K_{fEi}^m = K_{Di}^m\, 1/K_{Di}^m$.

Assuming that species m of nuclide $i-1$ decays to species of nuclide i, the equations for one-dimensional equilibrium transport are

$$\frac{\partial}{\partial t}(K_i^m c_i^m) + v\frac{\partial c_i^m}{\partial z} - D\frac{\partial^2 c_i^m}{\partial z^2} + \lambda_i K_i^m c_i^m = \lambda_{i-1} K_{i-1}^{\ell} c_{i-1}^{\ell} + \phi_i^m \ , \tag{5}$$

$$i = 1,2,\ldots \ , \quad m = 1,2,\ldots,n \ , \quad t > 0 \ , \quad -\infty < z < \infty \ ,$$

where K_i^m is the retardation coefficient of species m of nuclide i, v the water velocity, D the dispersion coefficient, λ_i the decay constant, and where $\phi_i^m(z,t)$ is a radioactive source of the species m of the nuclide i.

To simplify, we assume that a given radioelement is represented by a single radionuclide i, so that c_i^m can be replaced by the radionuclide concentration N_i^m. Substituting Eq. (3) into Eq. (5) and summing up the resultant equations, we have the transport equation for the reference species l of nuclide i:

$$\tilde{K}_i \frac{\partial N_i^l}{\partial t} + v\frac{\partial N_i^l}{\partial z} - D\frac{\partial^2 N_i^l}{\partial z^2} + \lambda_i \tilde{K}_i N_i^l = \frac{\lambda_{i-1}\tilde{K}_{E,i-1}\tilde{K}_{i-1}}{\tilde{K}_{Ei}} N_{i-1}^l + \frac{\phi_i}{\tilde{K}_{Ei}} \ , \tag{6}$$

$$i = 1,2,\ldots \ , \quad -\infty < z < \infty \ , \quad t > 0 \ ,$$

where $\tilde{K}_i$ is the effective retardation coefficient defined by

$$\tilde{K}_i = \left[K_i^l + \sum_{m=2}^{n} K_i^m \left(\prod_{j=1}^{m-1} K_{fEi}^j\right)\right] \Big/ \tilde{K}_{Ei} \ , \tag{7}$$

with

$$\tilde{K}_{Ei} = 1 + \sum_{m=2}^{n} \left(\prod_{j=1}^{m-1} K_{fEi}^j\right) \ . \tag{8}$$

For a band release resulting from dissolution of waste at z = 0, the source term $\phi_i(z,t)$ is given by

$$\phi_i(z,t) = \sum_{m=1}^{n} \phi_i^m = \frac{M_T^0}{T} B_i(t)\,\delta(z)\,[h(t) - h(t-T)] \ , \tag{9}$$

where M_T^0 is the total initial amount of waste material per unit cross-sectional area of water flow, T the leach time, and $B_i(t)$ the amount of nuclide i in the waste per unit amount of waste, as given by the Bateman equation.

Equation (6) is the same form as the transport equation for a single-species nuclide chain published elsewhere.[3] Thus, with the transformations of Eqs. (7) and (8), we can apply the general solution for the transport of a single-species nuclide chain.

In Fig. 1 the concentration profiles with two equilibrium species of ^{237}Np, with an assumed equilibrium constant $K_{Ef1}^1 = [Np^{(2)}]/[Np^{(1)}] = 0.7$, are compared with those of the same nuclide chain with a single weakly sorbing

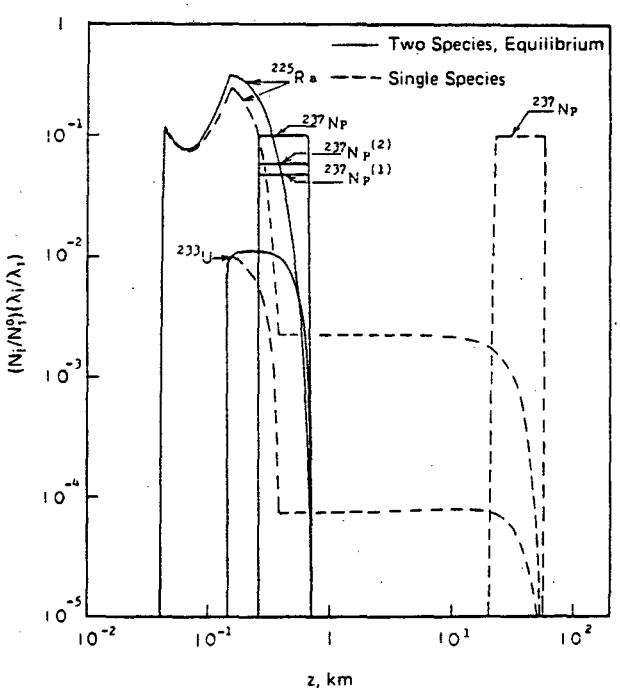

Fig. 1. Effects of mother nuclide with two species at equilibrium on the concentration profiles of a three-member decay chain, $^{237}Np \rightarrow {}^{233}U \rightarrow {}^{229}Th$ (^{225}Ra) at t = 50 000 yr [T = 30 000 yr, v = 100 m/yr, D = 0.1 m²/yr, $K_{Np}(1)$ = 100, $K_{Np}(2)$ = 10 000, K_U = 14 000, K_{Th} = 50 000, K_{Ra} = 500, K_{fE1}^1 = 0.7].

species of neptunium ($K^{1}_{Ef1} = 0$). The assumed values for other relevant parameters are shown in Fig. 1. Because of species equilibrium, chromatographic separation of the neptunium species does not occur. The effect of equilibrium with a more strongly sorbing species is to reduce the rate of transport of the entire neptunium band and of the neptunium daughters. Species equilibrium reduces the spread and increases the local maximum concentrations of the bands of the neptunium daughters.

1. M. D. HILL, "Analysis of the Effect of Variations in Parameter Values on the Predicted Radiological Consequences of Geologic Disposal of High-Level Waste," NRPB-R86 (June 1979).

2. T. H. PIGFORD, P. L. CHAMBRÉ, M. ALBERT, M. FOGLIA, M. HARADA, F. IWAMOTO, T. KANKI, D. LEUNG, S. MASUDA, S. MURAOKA, and D. TING, "Migration of Radionuclides Through Sorbing Media, Analytical Solutions—II," UCB-NE-4003, LBL-11616, Lawrence Berkeley Lab. (Oct. 1980).

3. M. HARADA, P. L. CHAMBRÉ, M. FOGLIA, K. HIGASHI, F. IWAMOTO, D. LEUNG, T. H. PIGFORD, and D. TING, "Migration of Radionuclides Through Sorbing Media, Analytical Solutions—I," LBL-10500, Lawrence Berkeley Lab. (Feb. 1980).

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