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HYDROGEOLOGIC TRANSPORT OF DECAY CHAINS WITH NONEQUILIBRIUM CHEMICAL SPECIES

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July 1981

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We have presented elsewhere[1,2] the general solution for the hydrogeologic transport of radionuclides in a decay chain of arbitrary length, in a one dimensional flow field, with local sorption equilibrium, and with a single chemical species for each radionuclide in the liquid or solid phases. Many of the important radionuclides, particularly the actinides, can exist as more than one chemical species in a given phase[3]. We have shown[2,4] that by appropriate transformations of species-dependent equilibrium and sorption constants our general solutions are applicable to multiple species if there is local chemical equilibrium between species. Depending upon the reaction rates between species, there is a possibility that local equilibrium between species in a given phase does not exist. This may be particularly important in laboratory experiments and in field tests of radionuclide transport. Here we present solutions for the transport of a radionuclide decay chain in which individual chemical species may not have reached local chemical equilibrium

in a given phase. The solution is illustrated for the decay chain $^{237}Np \rightarrow {}^{233}U \rightarrow$.

Let N_i^m and M_i^m be the space-time-dependent concentrations of the $\underline{m}$ chemical species of nuclide $\underline{i}$ in the water and solid phases respectively. Assuming one-dimensional transport in the z direction, the dispersion-free conservation equations for species $\underline{m}$ are:

$$\frac{\partial}{\partial t}\left(\varepsilon N_i^m\right) + v\frac{\partial}{\partial z}\left(\varepsilon N_i^m\right) + k_t s\left(N_i^m - \frac{M_i^m}{K_{Di}^m}\right) + \varepsilon\left(k_{fi}^{ml} N_i^m - k_{fi}^{lm} N_i^l\right) +$$

$$\varepsilon\left(\lambda_i N_i^m - \lambda_{i-1} N_{i-1}^n\right) = 0 \qquad (1)$$

$$\frac{\partial}{\partial t}\left[(1-\varepsilon)M_i^m\right] - k_t s\left(N_i^m - \frac{M_i^m}{K_{Di}^m}\right) + (1-\varepsilon)\left(k_{si}^{ml} M_i^m - k_{si}^{lm} M_i^l\right) +$$

$$(1-\varepsilon)\left(\lambda_i M_i^m - \lambda_{i-1} M_{i-1}^m\right) = 0 \qquad (2)$$

$$i = 1,2,\ldots, \quad m,l = 1,2,\ldots, \quad \lambda_o = 0, \quad t \geq 0, \quad 0 \leq z \leq \infty$$

where v is the water velocity, k_t is the coefficient for mass transfer between wate and solid phases, s is the interfacial area per unit volume of water plus solid, k_{fi}^{ml} and k_{si}^{ml} are first-order rate constants for chemical reactions from the $\underline{m}$ to $\underline{l}$ species, λ_i is the decay constant, K_{Di} is the distribution coefficient of species $\underline{m}$, and ε is the property of the medium.

The solutions will be illustrated for two chemical species of each radioelement in each phase, so that m,l = 1,2 and for local chemical equilibrium between phases, i.e., $M_i^m \rightarrow K_{Di}^m N_i^m$ and $k_t \rightarrow \infty$. The effects

of departures from local sorptive equilibrium have been analyzed separately[2]. The initial condition is:

$$N_i^m (z,0) = 0, \; z > 0, \; m = 1,2 \tag{3}$$

The time-dependent concentration boundary condition[4] at z = 0 is:

$$N_i^m (o,t) = B_i^m (t), \quad t > 0, \quad m = 1,2 \tag{4}$$

The general solution for a decay chain or arbitrary length, with each nuclide existing in two non-equilibrium species in a given phase, is expressed[2] in recursive form in terms of the above parameters. It is too long to be presented here.

To illustrate the migration behavior of two species, we apply the solution to the two-member decay chain $^{237}Np \rightarrow {}^{233}U \rightarrow$ to obtain the concentration profiles shown in Figure 1 for a band release, calculated at 50,000 yr after the beginning of waste dissolution. The caption of Figure 1 lists assumed values of the sorption retardation constants for each species of each nuclide, assumed values of the first-order reaction constants for the liquid (f) and solid (s) phases, and values of other parameters assumed for this calculation. It is assumed that no ^{233}U and only the strongly sorbing species $^{237}Np^1$ are initially present in the dissolving waste, resulting in an initial concentration N_{10} at the repository. Also shown, for comparison, are the concentration profiles for these four species calculated on the basis of local chemical equilibrium between species in a given phase.

With species equilibrium the concentration profile of each species of a radionuclide is proportional to the concentration profile of the

other species. In nonequilibrium the peak concentration of each species appears at the position depending upon the sorption retardation constant K_i for that species. The maximum total concentration of a radionuclide with species equilibrium is greater than the peak concentration of any individual species without equilibrium. The effect of nonequilibrium is to broaden the chromatographic band for each radionuclide and to attenuate its peak value, qualitatively similar to the effect of an unrealistically large dispersion constant.

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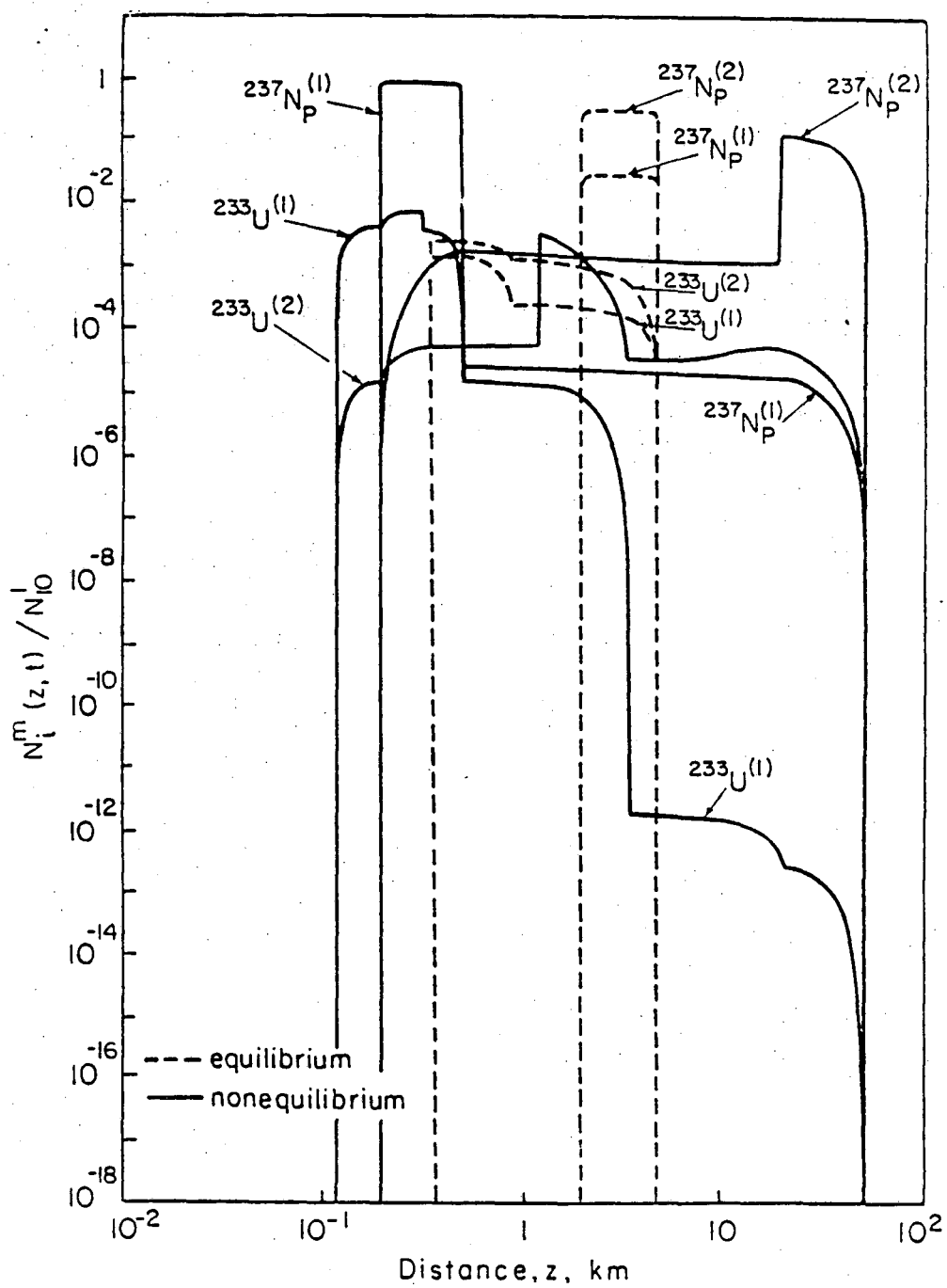

Figure 1. Comparison of species concentration profiles for the chain $^{237}Np \rightarrow {}^{233}U \rightarrow$ (t = 50,000 yr, leach time = 30,000 yr, $K_1^1 = 10{,}000$, $K_1^2 = 100$, $K_2^1 = 15{,}000$, $K_2^2 = 1{,}500$, $k_{f1}^{12} = 10^{-5}\ yr^{-1}$, $k_{f1}^{21} = 10^{-6}\ yr^{-1}$, $k_{f2}^{12} = 10^{-4}\ yr^{-1}$, $k_{f2}^{21} = 5 \times 10^{-5}\ yr^{-1}$, $k_{s1}^{12} = 10^{-7}\ yr^{-1}$, $k_{s1}^{21} = 10^{-6}\ yr^{-1}$, $k_{s2}^{12} = 10^{-6}\ yr^{-1}$, $k_{s2}^{21} = 5 \times 10^{-6}\ yr^{-1}$).

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