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SOLUBILITY LIMITED MIGRATION OF A RADIONUCLIDE CHAIN THROUGH A GEOLOGIC MEDIUM

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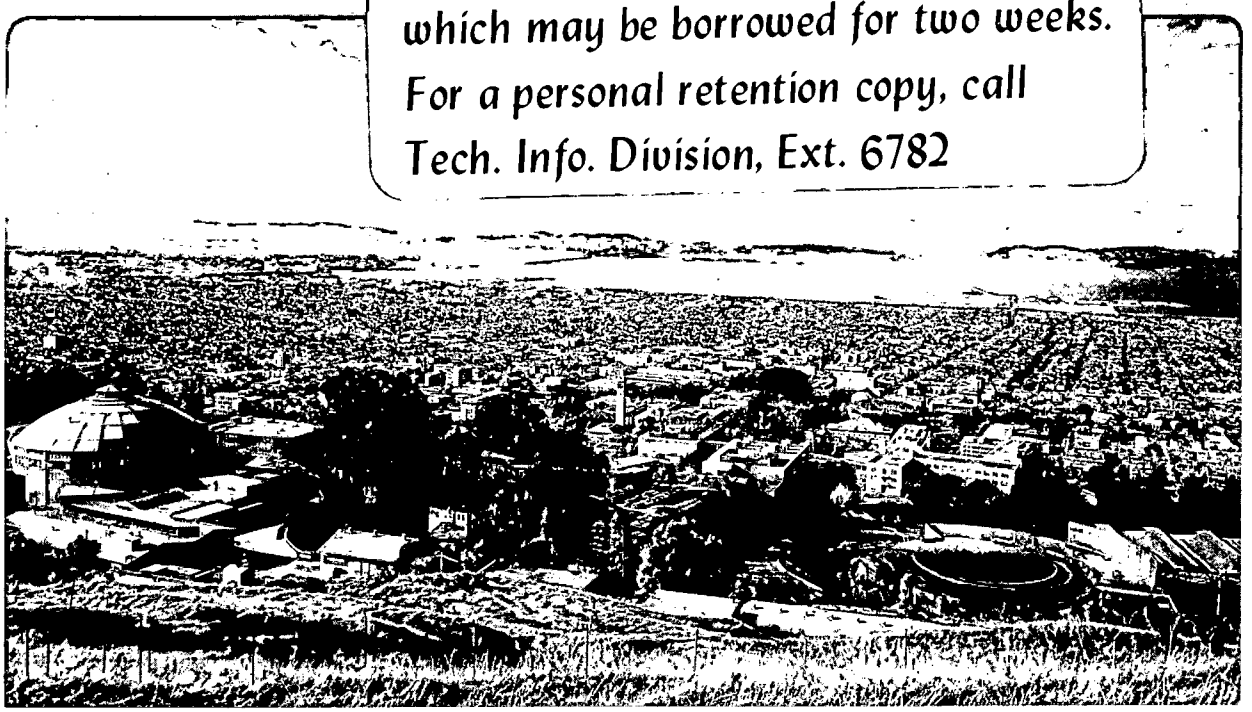

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SOLUBILITY LIMITED MIGRATION OF A RADIONUCLIDE CHAIN THROUGH A GEOLOGIC MEDIUM

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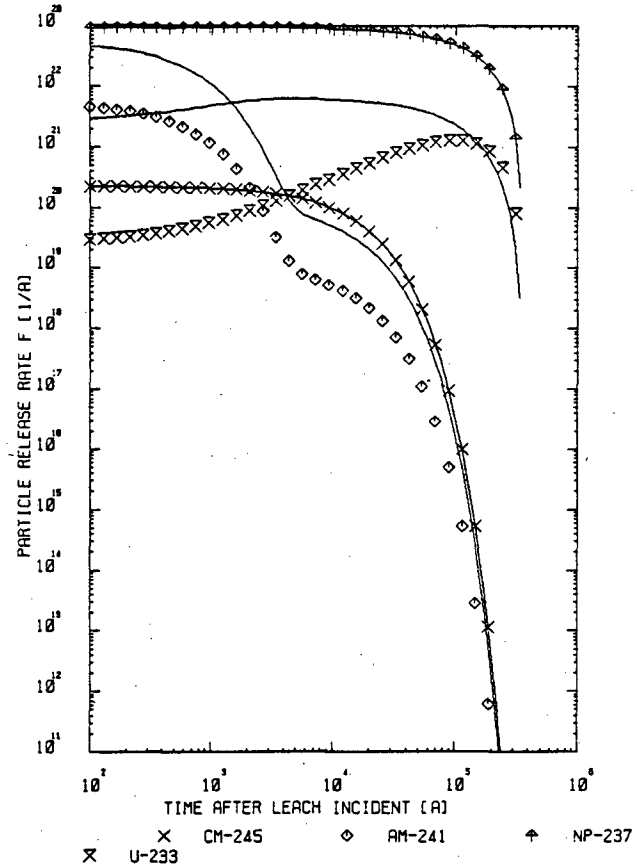

Fig. 1. Comparison with Hill et al. model (points).

Because the general model takes into account both processes—nuclide-dependent leaching and chemical dissolution of the waste matrix—it should give more realistic and mostly more conservative results than the simpler models used up to now.

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4. Solubility Limited Migration of a Radionuclide Chain Through a Geologic Medium,

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A solubility limit on the concentration of a radionuclide in groundwater is one of the most important barriers to the release of radionuclides from a geologic waste repository. For the first member of a decay chain migrating through a geologic medium of constant physicochemical properties, a solubility limit, if it occurs, imposes a boundary condition of saturation concentration at the surface of the dissolving waste.[1] For decay daughters not initially in secular equilibrium in the waste, the solubility limits, if they occur, will exist away from the waste location. Precipitates of these solubility limited daughter nuclides may be found distributed over finite regions in the surrounding geologic medium. We here develop a schematic approach to solve the hydrogeologic one-dimensional equilibrium transport of daughter radionuclides with solubility limits, and we demonstrate the effect of precipitation on the space-time-dependent concentrations of these daughter radionuclides in groundwater.

As a typical case, consider the two-member chain $^{234}U \rightarrow {}^{230}Th$. The waste is assumed to contain a finite amount of ^{234}U at the beginning of dissolution, but no ^{230}Th is initially present. The ^{234}U is assumed to dissolve without solubility limit. The waste matrix is assumed to dissolve at a constant rate. The solubility limit N_2^* of the ^{230}Th daughter and the initial concentration N_1^0 of the ^{234}U in the water adjacent to the waste at the beginning of dissolution are both specified. Also specified are the sorption retardation coefficients K_1 for the ^{234}U parent and K_2 for the ^{230}Th daughter. Dispersion is to be neglected and local chemical equilibrium assumed.

Understanding of the phenomena to be analyzed is aided by referring to Fig. 1, which shows the typical isopleths for the concentration N_2 of the daughter as a function of distance from the dissolving waste and time since the beginning of dissolution.[2] There are domains D1 and D2 free of precipitant and D3 wherein precipitation of the daughter nuclide occurs. In domain D1, the daughter concentration never reaches the saturation level, so the isopleths calculated for unlimited solubility are still valid. However, concentrations in D2 will be affected by precipitation in the region D3 nearer the waste.

As the decay of the migrating parent causes the daughter concentration to increase away from the dissolving waste, precipitation first begins at point A, when $^1N_2(z,t)$ first reaches the saturation concentration N_2. As the amount of daughter further increases, the inner edge of the precipitation zone first moves back toward the waste and the precipitation front moves outward, following the migration of the parent nuclide. By this process, the zone of precipitation broadens with time and later contracts, with its inner and outer edges following the path of bold-faced lines of Fig. 1. After the inner edge reaches the tangential point B, the precipitant formed nearer the waste then begins to redissolve and the inner edge begins to move outward. Point C locates the last of the precipitant.

The analysis herein is based on the expectation that the outer path AC of the precipitation front will be determined by the migration of the parent nuclide, which follows the path $z = vt/K_1$, where v is the groundwater velocity. The locus of the inner path $z = \psi(t)$, which describes the boundary between D1 and D3, is presently unknown and is to be determined by the ensuing analysis.

Neglecting dispersion, the aqueous concentration of the mother and daughter nuclides are governed by the following equation of one-dimensional equilibrium transport:

$$K_i \frac{\partial N_i}{\partial t} + v \frac{\partial N_i}{\partial z} + \lambda_i K_i N_i = \lambda_{i-1} K_{i-1} N_{i-1} \ , \qquad (1)$$

$$i = 1,2 \ , \quad t > 0 \ , \quad \lambda_0 = 0 \ .$$

Because the parent nuclide is assumed to dissolve without a solubility limit, the initial and boundary conditions, assuming a step release, are

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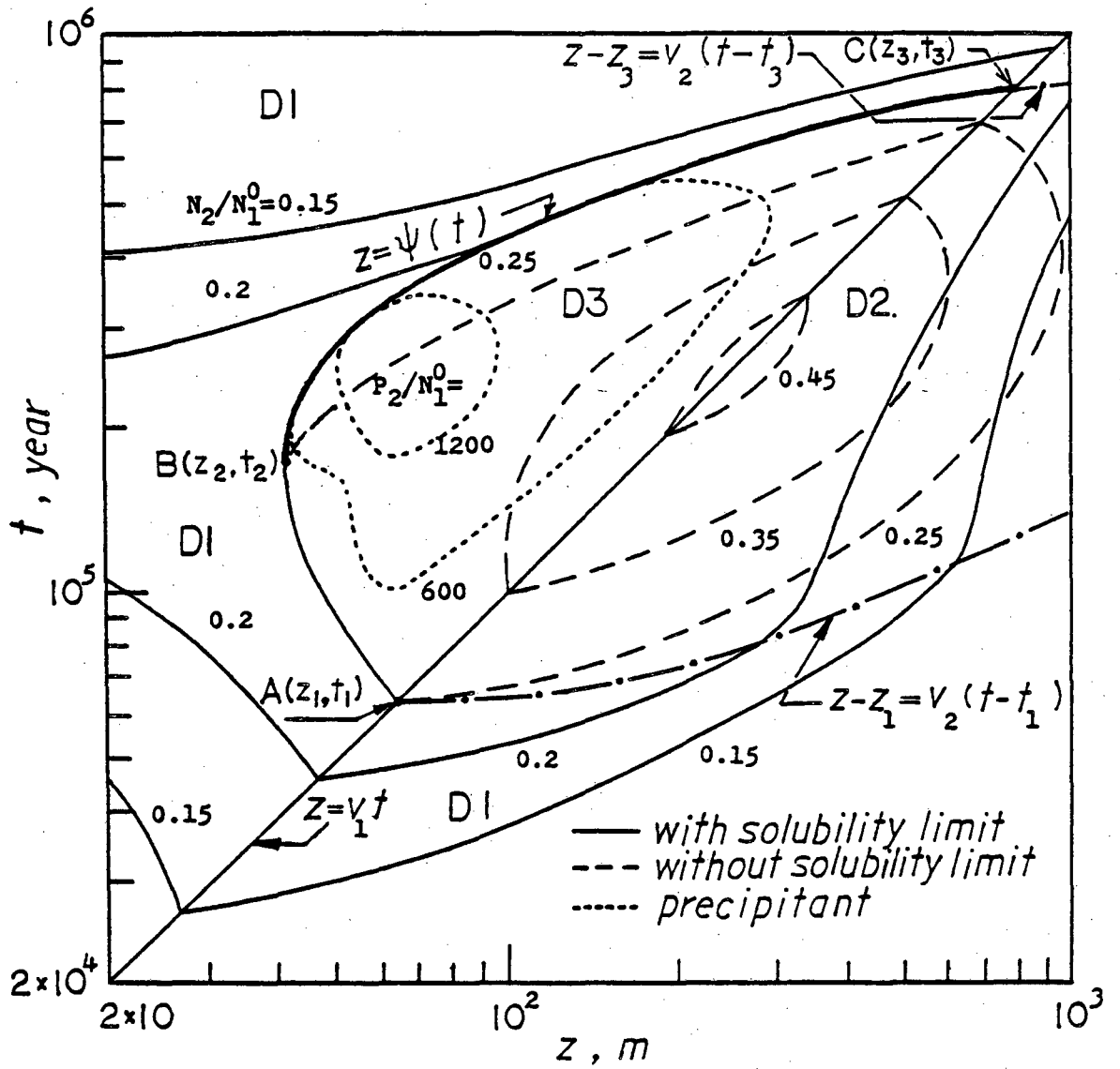

Fig. 1. Comparison between isopleths of relative concentration of daughter nuclide ^{230}Th with solubility limit and those of the nuclide without solubility limit, $^{234}U \rightarrow {}^{230}Th$ ($K_U = 10\,000$, $K_{Th} = 1000$, $v = 10$ m/yr, $N^*_{Th} = 0.25\ N^0_U$).

$$N_1(z,0) = 0, \qquad z > 0\ , \tag{2}$$

$$N_1(0,t) N_1^0 \exp(-\lambda_1 t)\ , \quad t > 0\ . \tag{3}$$

In domain D1, the initial and boundary conditions for the daughter with $N_2^0 = 0$ are

$$^1N_2(z,0) = 0\ , \quad Z > 0\ , \tag{4}$$

$$^1N_2(0,t) = N_1^0 \frac{\lambda_1}{\lambda_2 - \lambda_1} [\exp(-\lambda_1 t) - \exp(-\lambda_2 t)]\ , \quad t > 0\ . \tag{5}$$

Point A, at $(z_1 t_1)$, lies on the intersection of domain D1 and D2, so that

$$^1N_2(z_1,t_1) = {}^2N_2(z_1,t_1)\ . \tag{6}$$

Also, assuming that the outer boundary of the precipitation zone moves at the velocity v/K_1, then the moving point describes a path of the saturation concentration N_2^*:

$$^2N_2(vt/K_1,t) = N_2^*\ , \quad t_1 < t < t_3\ , \tag{7}$$

where t_3 is a coordinate at point C, where the last of the precipitate disappears. Because of the precipitate in domain D3,

$$^3N_2 = N_2^*\ , \quad z,t \in D3\ . \tag{8}$$

The concentration p_2 of precipitate, which exists only in domain D3, is governed by the material balance:

$$\frac{\partial p_2}{\partial t} + \lambda_2 p_2 = \lambda_1 K_1 N_1 - \lambda_2 K_2 N_2^*\ , \quad z,t \in D3\ . \tag{9}$$

The initial and boundary conditions for Eq. (9), which apply in domain D3, are

$$p_2(z,t_1) = 0\ , \tag{10}$$

because precipitation has only begun at (z_1,t_1), and

$$p_2(z,t^*) = 0\ , \quad t^* = zK_1/v\ , \quad z_1 < z < z_3\ , \tag{11}$$

because precipitation is first beginning along the path outward from point A described by $z = vt/K_1$. Also,

$$p_2(z,t^*) = 0 \ , \quad \text{along boundary AB} \ , \quad z_2 < z < z_1 \ . \quad (12)$$

The boundary between domains D1 and D3, along the inner path BC, is described by

$$z = \psi(t) \ , \quad (13)$$

where $\psi(t)$ is yet to be determined. Along this boundary of re-solution, the precipitate concentration within D3 is finite, at a value $p_2[\psi(t),t]$. Fluid enters the boundary at a concentration ${}^1N_2[\psi(t),t]$ and causes a dissolution at a rate

$$v\{N_2^* - {}^1N_2[\psi(t),t)]\} = p_2[\psi(t),t]\, dz/dt \ ,$$
$$\text{at } z = \psi(t) \ . \quad (14)$$

The solution of Eqs. (1), (2), and (3) for the parent nuclide and Eqs. (1), (4), and (5) for the daughter have already been given[3] for domain D1.

For domain D2, we obtain

$${}^2N_2(z,t) = N_2^* \exp\left[-\frac{\lambda_2}{v_2 - v_1}(z - v_1 t)\right] . \quad (15)$$

Integration of Eqs. (8) with aid of Eqs. (9) and (10) gives the space-time-dependent concentration of the precipitate:

$$p_2(z,t) = \int_{t^*}^{t} \exp[-\lambda_2(t-\theta)]\,[\lambda_1 K_1\, {}^1N_1(z,\theta) - \lambda_2 K_2 N_2^*]\, d\theta \ ,$$
$$D \in D3 \ . \quad (16)$$

The path $z = \psi(t)$ of the inner edge of the precipitation zone can be obtained by solving Eqs. (14) and (16) numerically.

The calculated isopleths of the concentration N_2 of ^{230}Th with an assumed solubility limit are shown as the solid lines in Fig. 1. The isopleths without solubility limit are shown as dashed lines. The maximum concentration originally located on a ridge line of $z = vt/K_1$ without a solubility limit is now reduced to the saturation level and spans a greater distance. In domains D2 and D3, the effect of the solubility limit is to reduce the maximum concentration at a given position and to delay the appearance of a given concentration. The isopleths of precipitate concentration are shown in Fig. 1 with dotted lines. The isopleths of both precipitate and dissolved concentration are discontinuous at the inner boundary BC between D1 and D2.

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5. Migration of Long Actinides Chains in Geologic Media, *D. Ting, P. L. Chambré, T. H. Pigford (Univ of California, Berkeley)*

There are two groups of radionuclides in high-level wastes that present potential hazard to the biosphere: the long-lived fission products (e.g., ^{129}I, ^{99}Tc, etc.) and the long actinide chains (e.g., ^{246}Cm–^{242}Pu–^{238}U–^{234}U–^{230}Th–^{226}Ra).

To accurately predict the transport of an actinide, it is necessary to consider its linkage to all its precursors through the decay chain. The modeling of the migration of these long actinide chains through geologic media described in the present study is restricted by the following assumptions:

1. The hydrological groundwater flow is time-independent, incompressible, and one-dimensional.
2. Dispersion effects are neglected.
3. The sorption reactions between nuclides in the liquid and the solid are in equilibrium.
4. Media properties characterizing soil, water, and radiochemistry are treated as isotropic and constant.

Subject to the above assumptions, the conservation equation for the nuclide concentration in the groundwater $N_i(z,t)$ of the i'th member of a actinide chain can be written as follows:

$$K_i \frac{\partial N_i}{\partial t} + V \frac{\partial N_i}{\partial z} + K_i \lambda_i N_i = K_{i-1} \lambda_{i-1} N_{i-1} \ , \quad i = 1,2,3,4 \ldots ,$$
$$\lambda_0 = 0 \ , \quad (1)$$
$$z > 0 \ , \quad t > 0 \ .$$

Here, K_i is the overall sorption constant, λ_i the decay constant, z the distance from the repository, V the constant groundwater velocity, and t the time after the release (leaching) starts.

The initial condition, at any point $z > 0$, is expressed by

$$N_i(z,0) = 0 \ ; \quad z > 0 \ . \quad (2)$$

The boundary condition can be represented by an arbitrary release function:

$$N_i(0,t) = N_i^0 \phi_i(t) \ , \quad t > 0 \ . \quad (3)$$

The solution to Eq. (1), subject to side conditions (2) and (3), has been obtained analytically[1] and can be written as

$$N_i(z,t) = N_i^0 \exp(-\lambda_i K_i \sigma)\phi_i(t - K_i\sigma) + \sum_{j=1}^{i-1} A_i^{(j)} N_j^0$$
$$\times \sum_{m=j}^{i} \frac{\exp(-\lambda_m K_m \sigma)}{B_m^{(j)}} \sum_{\substack{r=j \\ r \neq m}}^{i} D_{rm}^{(j)}$$
$$\times [g_{rm}(t) \circledast \phi_j(t)] \ . \quad (4)$$

Here,

$$N_i^0 = \frac{M_i^0}{QT} \ ; \quad \sigma = \frac{z}{v} \ , \quad (5)$$

and M_i^0 is the initial activity and Q the volumetric water flow. Then,

$$A_i^{(j)} = \prod_{r=j}^{i-1} \lambda_r K_r \ , \quad (6)$$

$$B_m^{(j)} = \prod_{\substack{r=j \\ r \neq m}}^{i} (K_r - K_m) \ , \quad (7)$$

$$D_{rm}^{(j)} = \left[\prod_{\substack{q=j \\ q \neq m \neq r}}^{i} (\Delta_{qm} - \Delta_{rm}) \right]^{-1} \ , \quad (8)$$

$$\Delta_{ij} = \frac{\lambda_i K_i - \lambda_j K_j}{K_i - K_j} \ . \quad (9)$$

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