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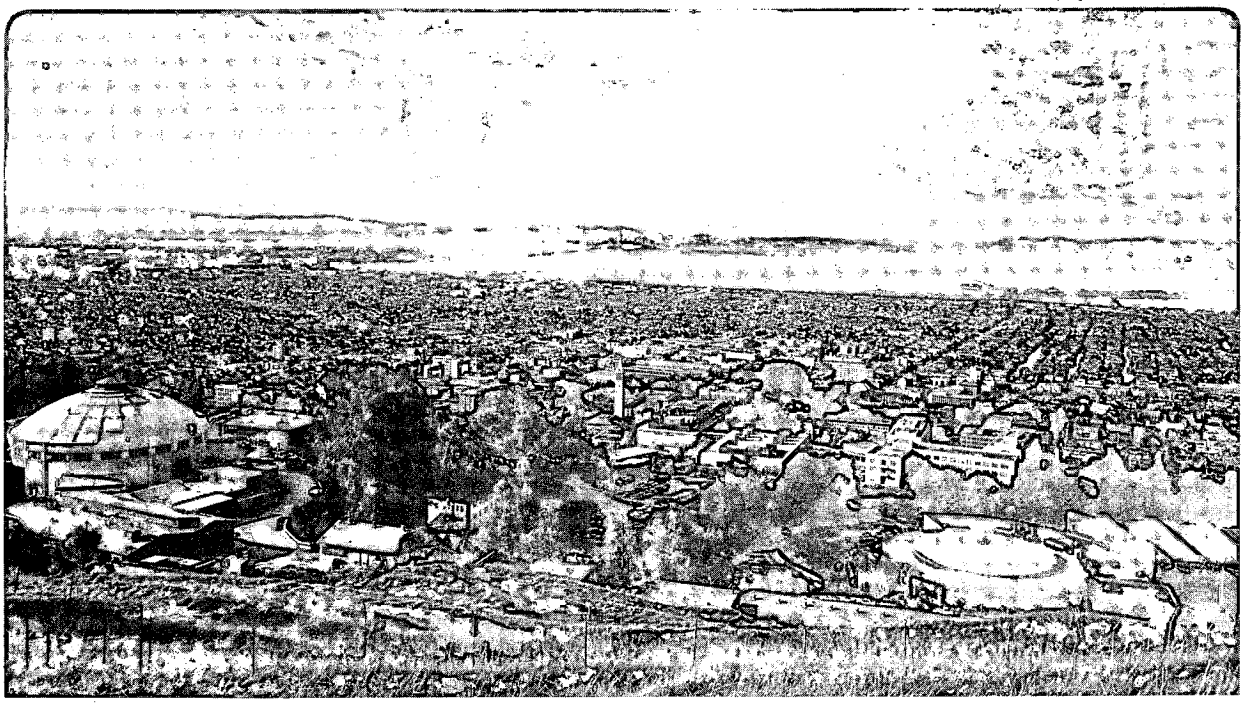

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DISSOLUTION/PRECIPITATION OF A TWO-MEMBER CHAIN AT A DISSOLVING WASTE MATRIX

W. Zhou, J. Ahn, W. W.-L. Lee, P. L. Chambré, and T. H. Pigford

Department of Nuclear Engineering
University of California

and

Earth Sciences Division
Lawrence Berkeley Laboratory
1 Cyclotron Road
Berkeley, California 94720

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Dissolution/Precipitation of a Two-Member Chain at a Dissolving Waste Matrix

W. Zhou, J. Ahn, W. W.-L. Lee, P. L. Chambré & T. H. Pigford
Lawrence Berkeley Laboratory & Department of Nuclear Engineering
University of California
Berkeley, CA 94720-0001, USA
415-642-6469

1. Introduction

When the matrix of a nuclear waste in porous rock dissolves in ground water, other species in the waste are also released. Some species, such as the actinides and rare-earths, are of such low solubility that they may precipitate as soon as they are dissolved, depending on the rate of matrix dissolution, their concentration in the waste solid, their solubilities, and the ground water transport rate. We have previously studied the solubility-limited dissolution of single species as controlled by the rate of advective mass transfer from the waste surface.[1] When the waste constituents include low-solubility members of a decay chain, the radioactive decay daughter can form a precipitate at the waste surface or in the rock away from the waste surface. Here we present a simplified analysis of the precipitate formation and dissolution of species in a two-member decay chain. For this purpose it is assumed that flowing ground water becomes saturated with the chemical species of the nuclides as it flows past the waste, resulting in a constant rate of solubility-limited dissolution of the waste matrix. Assuming congruent release of other waste constituents from the solid, the time-dependent amounts of precipitates of the first and second member of the decay chain at the waste surface can be calculated. Numerical illustrations for the $^{234}U \rightarrow {}^{230}Th$ chain from spent fuel are given in this paper. Full derivations are given elsewhere.[2]

2. Analysis

We consider one-dimensional transport through porous rock from an infinite plane source normal to the direction of water flow. Water flows unidirectionally at the same velocity throughout the medium. Retardation is treated by equilibrium sorption. Dispersion-free transport is assumed. The mass balance at the interface between waste and porous rock is shown schematically in Figure 1.

The governing equations for transport of a two-member decay chain are

$$K_1 \frac{\partial N_1}{\partial t} + v \frac{\partial N_1}{\partial z} + \lambda_1 K_1 N_1 = 0, \qquad z > 0, t > 0. \qquad (1)$$

$$K_2 \frac{\partial N_2}{\partial t} + v \frac{\partial N_2}{\partial z} + \lambda_2 K_2 N_2 = \lambda_1 K_1 N_1, \qquad z > 0, t > 0 \qquad (2)$$

where subscripts 1 and 2 refer to the mother and daughter nuclides respectively, and

$N_i(z,t)$ is the concentration of the ith member in the water phase in a porous medium at a distance z from the dissolution location at a time t after the start of dissolution, [kg-nuclide/m^3], i=1,2

K_i = sorption retardation coefficient for the ith member, i=1,2

λ_i = decay constant of the ith member [yr^{-1}], i=1,2

The aim of this paper is to find the mass rate of release per unit cross sectional area, ϕ_i; the mass of precipitates per unit cross sectional area, P_i; the concentration of the nuclides at the interface and in the field, $N_i(0,t)$, $N_i(z,t)$; and t_{Th}, the starting time of ^{230}Th precipitation; t_U^*, the duration of uranium precipitate; and t_{Th}^*, the duration of ^{230}Th precipitate.

For illustration, we assume a simplified dissolution model whereby the waste solid dissolves at a constant mass rate for a leach time T, releasing its waste constituents congruently. We assume a waste cylinder 4 m high and 0.5 m in diameter with 1.8 Mg of heavy metal, containing 1710 kg of ^{238}U, 0.329 kg of ^{234}U and 3.59×10^{-6} kg of ^{230}Th initially.[3] The waste is in a water-saturated repository where the rock porosity ϵ is 0.01 and ground water flows at a pore velocity v of 10 m/a. We assume a leach time T for the waste solid of 10^5 years and solubilities N^* for uranium and thorium of 10^{-6} kg/m^3 and 10^{-7} kg/m^3 respectively. Uranium released from the waste will initially precipitate due to the choice of solubilities.

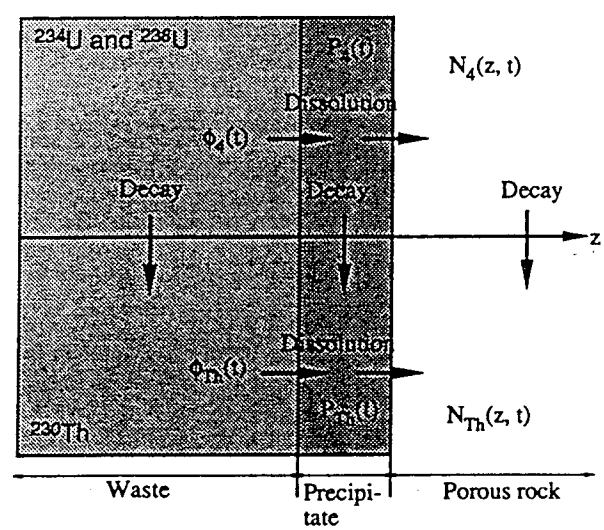

Fig. 1 A compartment model for the dissolution & precipitation of a two-member decay chain

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From a mass balance in the waste we find these initial concentrations that would result in the absence of solubility limits

$$N_8^\circ = 8.55 \times 10^2 \ kg/m^3 \tag{3}$$

$$N_4^\circ = 1.64 \times 10^{-5} \ kg/m^3 \tag{4}$$

$$N_{Th}^\circ = 1.80 \times 10^{-10} \ kg/m^3 \tag{5}$$

where the subscripts 4, 8 and Th stand for ^{234}U, ^{238}U and ^{230}Th respectively. Because $N_8^\circ + N_4^\circ > N_U^*$, the uranium solubility, uranium precipitates at $t = 0$ and continues until

$$t_U^* = 5.5 \times 10^9 \ \text{years} \tag{6}$$

For the purpose of calculating the duration of the uranium precipitate, we include the decay of ^{238}U, but we neglect the decay of ^{238}U in the formation of ^{234}U in calculating the latter's concentration. Assuming that ^{234}U and ^{238}U dissolve from the waste in the same ratio as they exist in the waste, we can write equations for the concentration at the interface

$$N_4(0,t) = N_U^* \frac{N_4^\circ}{N_8^\circ} e^{-\lambda_4 t}, \qquad 0 < t < T \tag{7}$$

$$N_4(0,t) = N_U^* \frac{N_4^\circ}{N_8^\circ} e^{-\lambda_4 t + \lambda_8 (t-T)}, \qquad T < t < t_U^* \tag{8}$$

$$N_4(0,t) = 0, \qquad t > t_U^* \tag{9}$$

The release function for the mother nuclide ^{234}U is

$$\phi_4(t) = v N_4^\circ e^{-\lambda_4 t} \{h(t) - h(t-T)\} \tag{10}$$

where $h(\cdot)$ is a Heaviside step function. Eq. (10) states that, in the absence of a solubility limit, ground water at velocity v would carry away the initial concentration of ^{234}U exposed at the interface, subject to decay, during the leach time. If we assume the isotopic ratio in the precipitate is the same as the waste, we can calculate the rate of formation of the precipitate of uranium

$$P_4(t) = v \frac{N_4^\circ}{N_8^\circ} (N_8^\circ - N_U^*) t e^{-\lambda_4 t} \qquad 0 \le t \le T \tag{11}$$

Eq. (11) states the conservation of mass at the interface. The excess of the initial concentration over the solubility that is not advected away is precipitated. Here because ^{238}U is much more abundant than ^{234}U, precipitation is controlled by the concentration difference of ^{238}U. Beyond the leach time, the amount of precipitate of ^{234}U

$$P_4(t) = \frac{N_4^\circ}{N_8^\circ} e^{-\lambda_4 t + \lambda_8 (t-T)} P_8(t), \qquad t > T \tag{12}$$

is directly related to the amount of precipitate of ^{238}U. Assuming $P_8(t) \gg P_4(t)$, $P_8(t)$ is given by

$$P_8(t) = vT(N_8^\circ - N_U^*) e^{-\lambda_8 (t-T)} - \frac{v N_U^*}{\lambda_8} (1 - e^{-\lambda_8 (t-T)}), t > T \tag{13}$$

This completes the set of boundary conditions needed to solve the governing equation for the concentration of the mother nuclide ^{234}U everywhere, and a full solution can be given

$$N_4(z,t) = N_U^* \frac{N_4^0}{N_8^0} e^{-(\lambda_4/v_1)z} \{ e^{-\lambda_4 (t - z/v_1)} [h(t - \frac{z}{v_1}) - h(t - T - \frac{z}{v_1})]$$
$$+ e^{-\lambda_4 (t - z/v_1) + \lambda_8 (t - T - z/v_1)} [h(t - T - \frac{z}{v_1}) - h(t - t_U^* - \frac{z}{v_1})] \}, \quad \begin{matrix} z > 0 \\ t > 0 \end{matrix} \tag{14}$$

where $v_1 = v/K_U$ is the migration speed, the pore velocity divided by the retardation coefficient of uranium.

Now we are ready to deal with the daughter nuclide ^{230}Th. At $t = 0$ ^{230}Th is not at solubility so no precipitate of ^{230}Th exists initially. The release rate of ^{230}Th from the waste is also the dissolution rate, and is

$$\phi_{Th}(t) = v N_{Th}^\circ e^{-\lambda_{Th} t} + \frac{v N_4^\circ \lambda_4}{\lambda_{Th} - \lambda_4} \{ e^{-\lambda_4 t} - e^{-\lambda_{Th} t} \}, 0 \le t \le T \tag{15}$$

Using (15) to solve the following equation for the time t_{Th}, that precipitation of ^{230}Th begins at the waste wurface

$$N_{Th}(0,t) = \frac{\phi_{Th}}{v} + \frac{\lambda_4 P_4(t)}{v} = N_{Th}^* \tag{16}$$

we get

$$t_{Th} = 1088 \ \text{yr}$$

The precipitation of ^{230}Th starts well before the end of the leach time. To determine the duration of this ^{230}Th precipitate we solve for a zero of

$$P_{Th}(t) = v e^{-\lambda_{Th} t} N_4^\circ \lambda_4$$
$$\left(\{1 - \frac{N_U^*}{N_8^\circ}\} \frac{t e^{(\lambda_{Th} - \lambda_4)t} - t_{Th} e^{(\lambda_{Th} - \lambda_4) t_{Th}}}{\lambda_{Th} - \lambda_4} \right.$$
$$\left. - \frac{t - t_{Th}}{\lambda_{Th} - \lambda_4} + \frac{N_U^*}{N_8^\circ} \frac{e^{(\lambda_{Th} - \lambda_4)t} - e^{(\lambda_{Th} - \lambda_4) t_{Th}}}{(\lambda_{Th} - \lambda_4)^2} \right)$$
$$- \frac{v N_{Th}^*}{\lambda_{Th}} [1 - e^{-\lambda_{Th}(t - t_{Th})}], \qquad t_{Th} \le t \le T \tag{17}$$

and obtain

$$t_{Th}^* = 1.5 \times 10^6 \ \text{yr}$$

as the end of the ^{230}Th precipitate. Thus the ^{230}Th precipitate lasts longer than the leach time and we need a modified version of eq. (17) to serve as the source term for ^{230}Th until the end of the uranium precipitate

$$P_{Th}(t) = P_{th}(T) e^{-\lambda_{Th}(t-T)} - \frac{v N_{Th}^*}{\lambda_{Th}} [1 - e^{-\lambda_{Th}(t-T)}] + v e^{-\lambda_{Th} t} N_4^\circ \lambda_4$$
$$\times \left(T + \frac{N_U^*}{N_8^\circ} \frac{1}{\lambda_{Th} - \lambda_4} \right) \frac{e^{(\lambda_{Th} - \lambda_4)t} - e^{(\lambda_{Th} - \lambda_4)T}}{\lambda_{Th} - \lambda_4}$$
$$- v e^{-\lambda_{Th} t} N_4^\circ \lambda_4 \frac{N_U^*}{N_8^\circ} \left(\frac{t e^{(\lambda_{Th} - \lambda_4)t} - T e^{(\lambda_{Th} - \lambda_4)T}}{\lambda_{Th} - \lambda_4} \right), T \le t \le t_U^* \tag{18}$$

After t_{Th}^*, $P_{Th}(t) = 0$. Using the above we can obtain the interface concentration of ^{230}Th

$$N_{Th}(0,t) = \frac{\phi_{Th}}{v} + \frac{\lambda_4 P_4(t)}{v}, \qquad 0 < t \le t_2 \tag{19a}$$

$$N_{Th}(0,t) = N_{Th}^*, \qquad t_2 \le t \le t_2^* \tag{19b}$$

$$N_{Th}(0,t) = \frac{\lambda_4 P_4(t)}{v}, \qquad t_2^* \le t \le t_U^* \tag{19c}$$

$$N_{Th}(0,t) = 0, \qquad t \ge t_U^* \tag{19d}$$

Eq. (19a) states that before the start of ^{230}Th precipitation, the interface concentration is controlled by the rate of waste dissolution, advection, and decay from the precipitate of ^{234}U, the mother

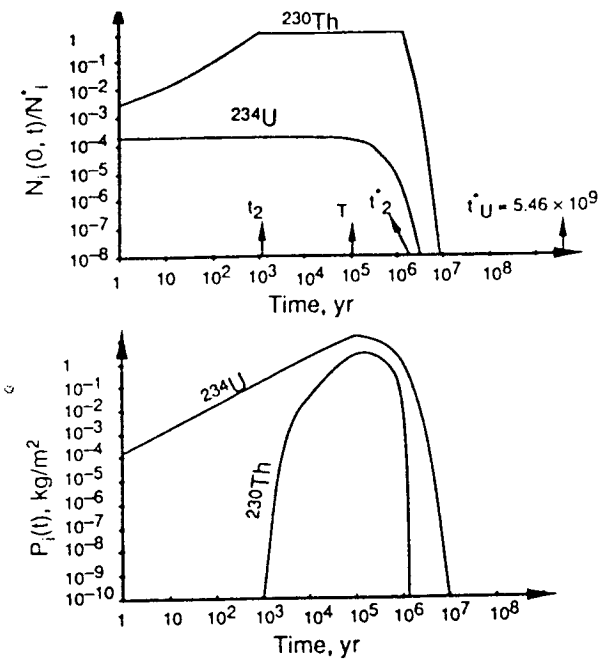

Fig. 2 Normalized concentrations and amounts of precipitates of the $^{234}U \rightarrow ^{230}Th$ chain from spent fuel, at the interface

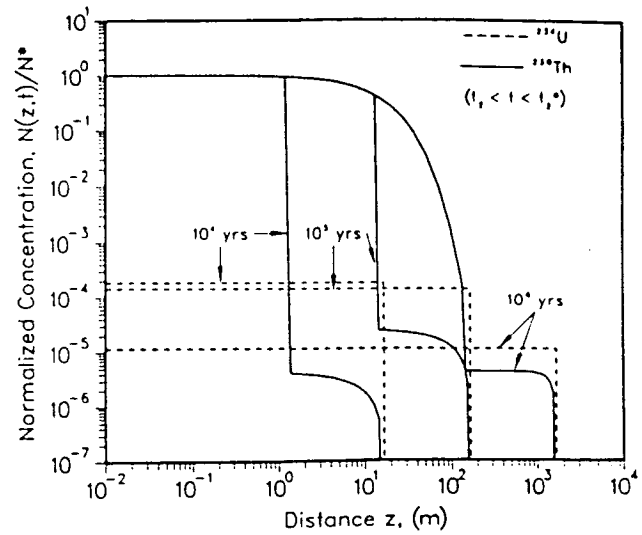

Fig. 3 Normalized concentrations of the $^{234}U \rightarrow ^{230}Th$ chain in rock at 10^4, 10^5, 10^6 years

nuclide. In the period of ^{230}Th precipitation, the interface concentration is saturation, eq. (19b). After the ^{230}Th precipitate has disappeared but while the uranium precipitate still remains, the interface concentration is controlled by the decay from the precipitate of the mother nuclide and advection, eq. (19c). Finally, after all precipitates have disappeared, there is no ^{230}Th at the interface, eq. (19d).

The normalized concentrations at the interface and amounts of precipitates of ^{234}U and ^{230}Th are shown in Figure 2. The equations for $N_{Th}(z,t)$ are very lengthy. They are given in Reference 2 but not reproduced here. Figure 3 shows the far-field concentrations of ^{234}U and ^{230}Th in the critical period when there is ^{230}Th precipitate at the interface, calculated using dispersion-free one-dimensional transport, using a previously derived analytic solution[4] and the data in Table I. Actual numerical outputs given in Reference 2 show that ^{230}Th concentrations in the field do not reach saturation.

Table I. Properties of the $^{234}U \rightarrow ^{230}Th$ chain.

	^{238}U	^{234}U	^{230}Th
Decay constant, 1/a	1.54×10^{-10}	2.81×10^{-6}	8.66×10^{-6}
Sorption coefficient, cm^3/g	20†	20†	250†
Retardation coefficient*	6,000	6,000	74,300
Migration speed, m/a	1.67×10^{-3}	1.67×10^{-3}	1.35×10^{-4}

*$K = 1 + \rho K_D(1-\epsilon)/\epsilon$, rock density $\rho = 3.0$ g/cm.^{3} † Ref. 5.

Conclusion

We have presented a simplified analysis of the dissolution, precipitation and transport of a two-member decay chain with advection as the only transport mechanism. We show the analytic solutions for the various fluxes such as dissolution rates, precipitation rates; times for the precipitate existence; and nuclide concentration fields. The numerical illustration used the $^{234}U \rightarrow ^{230}Th$ chain from spent fuel.

An important limitation of this analysis is that advection was assumed to be the only mode of transport. In several other studies, we have determined that in typical U. S. repository environments, ground water velocity may be so low that diffusive-advective transport may be the determinant of dissolution rates.[6] A more realistic model would be to include a diffusive term in the governing equations.

References

1. 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," *LBL-11616*, Lawrence Berkeley Laboratory (1980).
2. W. ZHOU, J. AHN, W. W.-L. LEE, P. L. CHAMBRÉ, and T. H. PIGFORD, "Dissolution, Precipitation and Transport of a Two-Member Decay Chain," *LBL-25243*, Lawrence Berkeley Laboratory (1988).
3. J. W. RODDY, H. C. CLAIBORNE, R. C. ASHLINE, P. J. JOHNSON and B. T. RHYNE, "Physical and Decay Characteristics of Commercial LWR Spent Fuel," *ORNL/TM-9591/V1&R1*, Oak Ridge National Laboratory (1986).
4. 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 Laboratory (1980).
5. J. RELYEA and M.I. WOOD, "An Analytical One-Dimensional Model for Predicting Waste Package Performance," *SD-BWI-TI-232*, Rockwell (1984).
6. P. L. CHAMBRÉ, T. H. PIGFORD, Y. SATO, A. FUJITA, H. LUNG, S. ZAVOSHY, and R. KOBAYASHI, "Analytical Performance Models," *LBL-14842*, Lawrence Berkeley Laboratory (1982).

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