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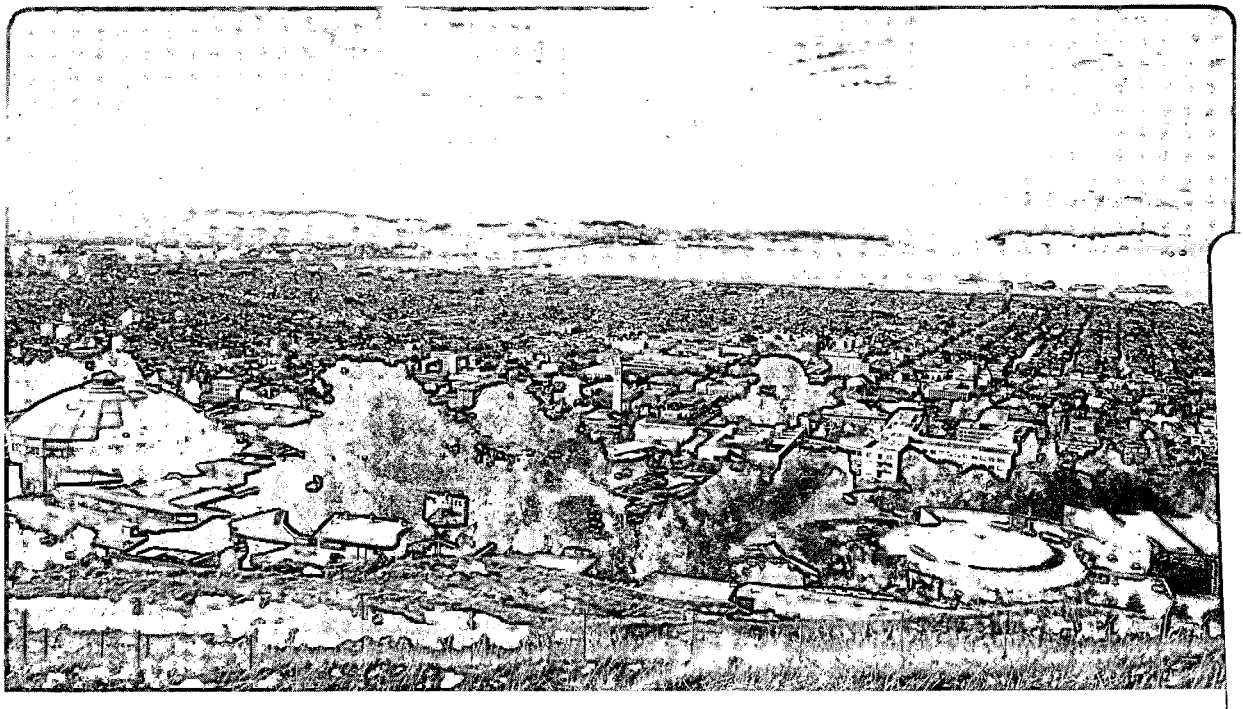
Equations for Predicting Release Rates for Waste Packages in Unsaturated Tuff

M.M. Sadeghi, T.H. Pigford, P.L. Chambré, and W.W.-L. Lee

August 1990



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Equations for Predicting Release Rates for Waste Packages in Unsaturated Tuff

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1. INTRODUCTION

Nuclear waste will be placed in the potential repository at Yucca Mountain in waste packages. Spent fuel assemblies or consolidated fuel rods and borosilicate glass in steel pour canisters will be enclosed in sealed containers. The waste package consists of the waste form, the cladding on spent fuel or the defense-waste pour canister, and the outside container. Current design calls for the waste packages to be surrounded by an air gap.

Although the waste package is generally not seen as the primary barrier for nuclear waste isolation, it must in fact meet specific regulatory requirements: substantially complete requirement and release-rate from the engineered barrier system [USNRC 1983]. This report gives derivations of equations for predicting releases rates.

We consider the release of three types of species: solubility-limited species, species released congruent with solid-solid alteration of spent-fuel matrix or borosilicate glass, and readily soluble species from the fuel-cladding gap, gas plenum, and readily accessible grain boundaries. We develop analytic expressions for the release rates of individual constituents from each of these mechanism. For a given species and for given parameters, the mechanism that results in the lowest predicted release rate is to be adopted as the rate-controlling mechanism for that species. Some of the equations are newly derived for this report, others are restated from earlier work. Release rates have been calculated for key radionuclides in a companion report [Sadeghi *et al.* 1990a]. We consider gaseous releases separately [Light *et al.* 1990].

2. WATER-CONTACT MODES

We consider two modes of water contact that lead to the release of radionuclides.

2.1 The Wet-Drip Water Contact Mode

First we consider the dripping of water from overhead rock onto waste packages [O'Connell and Drach 1986]. This dripping may happen because the change in rock permeability may divert water into fractures that intersect the borehole. Drips are assumed to penetrate cracks in failed container and to dissolve radionuclides as the radionuclide solution slowly rises in the container and finally overflows through other cracks and penetrations. Overflow of contaminated water is assumed to occur only near the top of the container. The contaminated water drips to the rock below. Water within the container is always well mixed from diffusion and thermal convection. We refer to this as the "wet-drip water-contact mode."

2.2 The Moist-Continuous Water-Contact Mode

The wet-drip mode assumes that the air-filled annulus surrounding a waste package precludes pathways for diffusive release of dissolved species. However, there can exist pathways for release by liquid diffusion if a waste package contacts the surrounding rock by physical displacement, if the annulus becomes filled with sediments and rubble, or if the repository horizon becomes water saturated [Pigford and Lee 1989]. Equations applicable to all three situations are presented here.

We assume that water has filled a failed container, and we conservatively neglect mass-transfer resistance from Zircaloy fuel cladding and from the residual container material and corrosion products. For the expected ground-water velocities, and for the diffusion coefficients assumed here for intact rock, mass-transfer is predicted to occur predominantly by molecular diffusion in pore liquid in the rock matrix [Pigford, Chambré, and Lee 1990]. Under these conditions the release rate is finite at zero velocity and is insensitive to any but very large increases in water velocity.

We conservatively assume that all moisture in the intact rock is in interconnected water-filled pores, with a pore-liquid diffusion coefficient given by that for a liquid continuum. As a result of the low effective diffusion coefficient for unsaturated rubble, with air in void spaces not occupied by rubble, the predicted mass transfer rates will be far below what could occur if the repository were saturated or if the degraded waste container were in close contact with consolidated or intact rock. Our analyses are constructed to

be applicable to the unsaturated environment, so this particular type of contact is more aptly termed the "moist-continuous water-contact mode," and is so referred to herein. The equations are also applicable to direct contact between waste and rock and to a water-saturated annulus, by specifying zero thickness of the annulus and suitably large values of the effective diffusion coefficient in the annulus.

3. EQUATIONS FOR THE WET-DRIP WATER-CONTACT MODE

We derive analytic equations for the release of three types of species. Figure 1 is a schematic of a waste package in the wet-drip contact mode.

3.1 Solubility-Limited Species

We assume here that when spent fuel rods or borosilicate glass are in contact with water, the waste constituents of the fuel are in chemical solubility equilibrium with the water. The concentration of each dissolved elemental species is at a maximum value given by the solubility of that species. For a low-solubility species, the release rate after container overflow and before all of the element has dissolved is the product of the volumetric drip rate Q, the elemental solubility C_{se}, and the time-dependent isotope fraction of that species $n_i(t)/n_e(t)$.

$$\dot{m}_i(t) = \begin{cases} 0, & 0 \le t \le t_2 \\ C_{se}\frac{n_i(t)}{n_e(t)}Q, & t_2 \le t \le t_3 \end{cases} \tag{1}$$

where
C_{se} is the elemental solubility (M/L^3),
Q is the volumetric flow rate of water into and out of the container (L^3/t),
$\dot{m}_i(t)$ is the mass release rate of the species (M/t),
$n_i(t)$ is the concentration of the species in the undissolved solid (M/L^3),
$n_e(t)$ is the concentration of the element in the undissolved solid (M/L^3),
t_2 is the time after emplacement when the container is full of water (t),
t_3 is the time when all of the element has dissolved (t).

If we take t_1 to be the time after emplacement that water first enters the failed container, $t_2 - t_1$ will be the time for the container to fill. Figure 2 shows a time-line of events. After dissolution of all the element, fresh water dilutes the container contents. The governing equation for the rate of change of species concentration $N_i(t)$ in the water, multiplied by $V(t_2)$, the volume of water when the container is full, is

$$V(t_2)\frac{dN_i(t)}{dt} = -N_i(t)V(t_2)\lambda_i - QN_i(t), \qquad t_3 \le t \le \infty \tag{2}$$

The initial condition is

$$N_i(t_3) = C_{se}\frac{n_i(t_3)}{n_e(t_3)} \tag{3}$$

After solving for $N_i(t)$ in (2), we multiply the result by Q to obtain the species release rate

$$\dot{m}_i(t) = QC_{se}\frac{n_i(t_3)}{n_e(t_3)}\exp\{[-\lambda_i - Q/V(t_2)](t - t_3)\}, \qquad t_3 \le t \le \infty \tag{4}$$

Considering a solubility-limited element containing j isotopes, each with a decay constant λ_i and initial concentration n_i^0, and ignoring decay precursors, the isotope fraction in the undissolved waste at time t is

$$\frac{n_i(t)}{n_e(t)} = \frac{n_i^0 e^{-\lambda_i t}}{\sum_{i=1}^{j} n_i^0 e^{-\lambda_i t}}, \qquad t \ge 0 \tag{5}$$

If we multiply the numerator and the denominator on the right hand side of (5) by the waste solid volume, we get

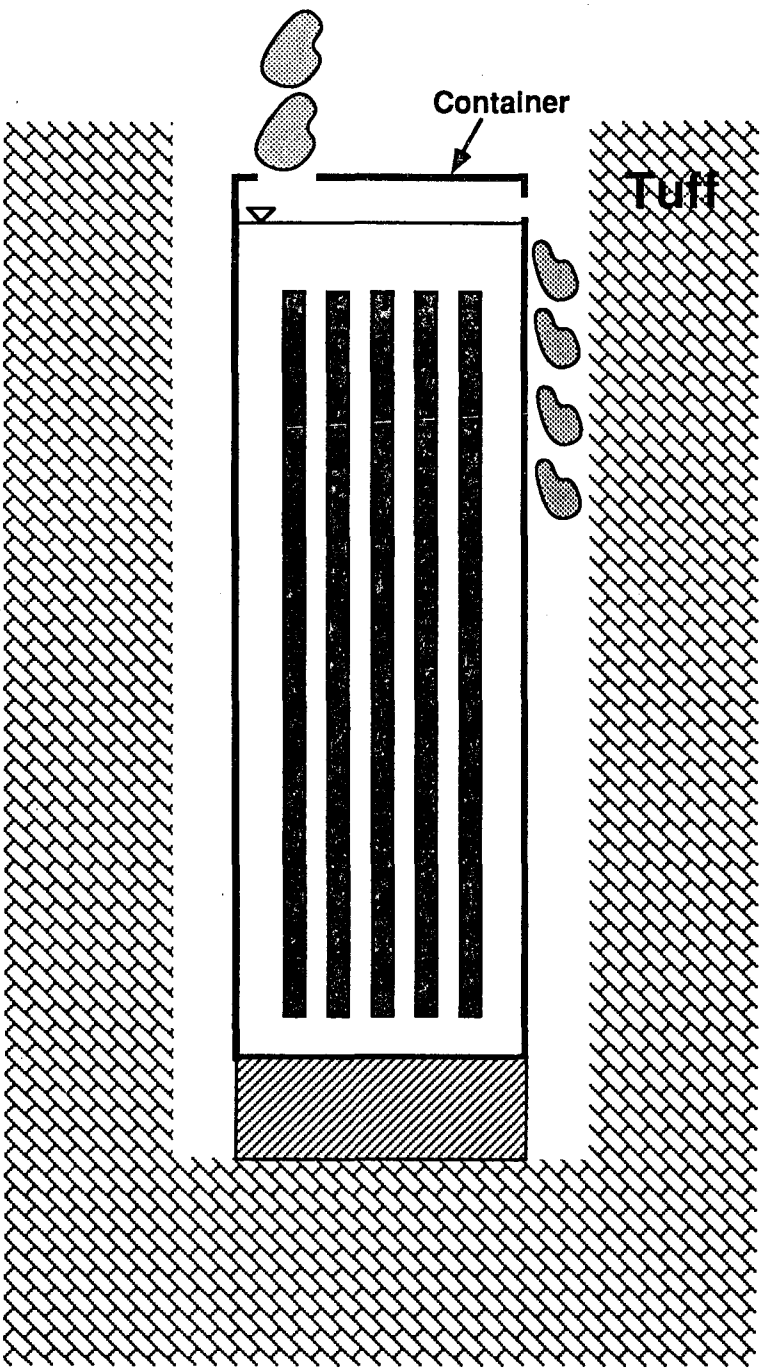

Figure 1. The Wet-Drip Water Contact Mode

$$\frac{n_i(t)}{n_e(t)} = \frac{M_i^0 e^{-\lambda_i t}}{\sum_{i=1}^{j} M_i^0 e^{-\lambda_i t}}, \qquad t \geq 0 \tag{6}$$

where M_i^0 is the initial inventory of the isotope. It is assumed that there is no preferential leaching (dissolution) of any of the species from the undissolved solid. To get the USNRC-defined fractional release rate of each radionuclide, based on its 1000-year inventory $M_i^\star$, we divide $\dot{m}_i(t)$ in equations (1) and (4) by $M_i^\star$

$$f_i(t) = \frac{\dot{m}_i(t)}{M_i^\star} = \begin{cases} 0, & 0 \leq t \leq t_2 \\ \frac{C_{se}}{M_i^\star} \frac{M_i^0 e^{-\lambda_i t}}{\sum_{i=1}^{j} M_i^0 e^{-\lambda_i t}} Q, & t_2 \leq t \leq t_3 \\ \frac{QC_{se}}{M_i^\star} \frac{M_i^0 e^{-\lambda_i t_3}}{\sum_{i=1}^{j} M_i^0 e^{-\lambda_i t_3}} \exp\{[-\lambda_i - Q/V(t_2)](t - t_3)\}, & t_3 \leq t \leq \infty \end{cases} \tag{7}$$

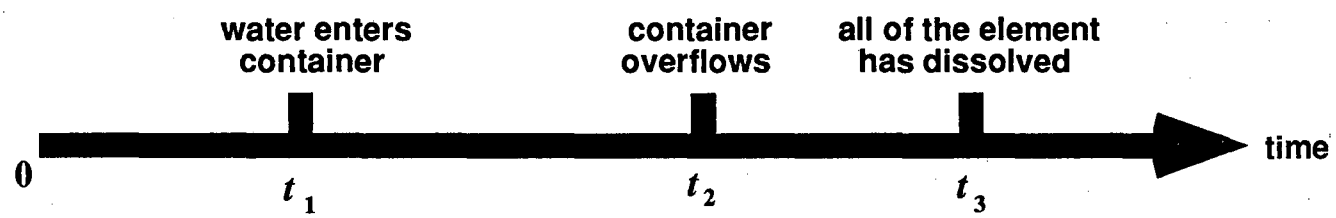

Figure 2. Sequence of Events for Solubility-Limited Wet Drip Contact

Here $M_i^\star$ is to be calculated for waste without dissolution, correcting only for radioactive decay. We obtain $t_2 - t_1$, the time for the container to fill, by dividing the volume of the water in the filled container $V(t_2)$ by Q, which is the velocity times cross-sectional area of the waste package,

$$t_2 - t_1 = \frac{V(t_2)}{Q} \tag{8}$$

3.2 Solubility-limited Release of a Three-member Decay Chain

Actinides in nuclear fuel are primarily part of radioactive decay chains. However, most analysis of release rates have considered only single species. For a three-member decay chain, we assume that the first member of the chain is limited by its elemental solubility. The two daughters are assumed to dissolve congruently with the dissolution of the first member of the chain.

To obtain the fractional release rate of each member of a three-member decay chain, we start by writing the mass release rate of the first chain member from the engineered barrier system into the rock in the time interval $t_2 \leq t \leq t_3$ as given by the second relation in equation (1)

$$\dot{m}_1(t) = C_{se} \frac{n_1(t)}{n_e(t)} Q, \qquad t_2 \leq t \leq t_3 \tag{9}$$

with

$$\frac{n_1(t)}{n_e(t)} = \frac{n_1^0 e^{-\lambda_1 t}}{\sum_{i=1}^{3} n_i^0 e^{-\lambda_i t}}, \qquad t \geq 0 \tag{10}$$

Because the two daughters are assumed to dissolve congruently with the dissolution of the first member of the chain, we write the dissolution rate of the congruently dissolved species 2 at time t, $\dot{m}_2(t)$, in terms of

the dissolution rate of the first member into the rock $\dot{m}_1(t)$, the concentration of the first member in the waste $n_1(t)$ (M/L^3), and the concentration of the second member in the waste $n_2(t)$ (M/L^3)

$$\dot{m}_2(t) = \dot{m}_1(t)\frac{n_2(t)}{n_1(t)}, \qquad t_2 \le t \le t_3 \tag{11}$$

With $\dot{m}_1(t)$ from equation (9) we get

$$\dot{m}_2(t) = C_{se}Q\frac{n_2(t)}{n_e(t)}, \qquad t_2 \le t \le t_3 \tag{12}$$

To get an expression for $n_2(t)$, we know species 2 is produced from species 1; therefore, the differential equation for the concentration of species 2 is

$$\frac{dn_2(t)}{dt} = -\lambda_2 n_2(t) + \lambda_1 n_1(t), \qquad t \ge 0 \tag{13}$$

With the initial condition

$$n_2(0) = n_2^0 \quad \text{known} \tag{14}$$

Equation (13) has the solution

$$n_2(t) = n_2^0 e^{-\lambda_2 t} + \frac{n_1^0\lambda_1}{\lambda_2 - \lambda_1}\left(e^{-\lambda_1 t} - e^{-\lambda_2 t}\right), \qquad t \ge 0 \tag{15}$$

We substitute (15) into (12) to get

$$\dot{m}_2(t) = C_{se}Q\frac{n_2^0 e^{-\lambda_2 t} + \frac{n_1^0\lambda_1}{\lambda_2-\lambda_1}\left(e^{-\lambda_1 t} - e^{-\lambda_2 t}\right)}{n_e(t)}, \qquad t_2 \le t \le t_3 \tag{16}$$

We get the mass release rate of the third member of the decay chain by writing

$$\dot{m}_3(t) = \dot{m}_1(t)\frac{n_3(t)}{n_1(t)}, \qquad t_2 \le t \le t_3 \tag{17}$$

which is equivalent to

$$\dot{m}_3(t) = C_{se}Q\frac{n_3(t)}{n_e(t)}, \qquad t_2 \le t \le t_3 \tag{18}$$

We obtain $n_3(t)$ by writing a differential equation for the third member

$$\frac{dn_3(t)}{dt} = -\lambda_3 n_3(t) + \lambda_2 n_2(t), \qquad t \ge 0 \tag{19}$$

with the initial condition

$$n_3(0) = n_3^0 \quad \text{known} \tag{20}$$

The solution to (19) is

$$n_3(t) = n_3^0 e^{-\lambda_3 t} + \frac{n_2^0\lambda_2}{\lambda_3 - \lambda_2}\{e^{-\lambda_2 t} - e^{-\lambda_3 t}\} + \frac{n_1^0\lambda_1\lambda_2}{(\lambda_2 - \lambda_1)(\lambda_3 - \lambda_1)}\{e^{-\lambda_1 t} - e^{-\lambda_3 t}\}$$

$$-\frac{n_1^0\lambda_1\lambda_2}{(\lambda_2 - \lambda_1)(\lambda_3 - \lambda_2)}\{e^{-\lambda_2 t} - e^{-\lambda_3 t}\}, \qquad t \ge 0 \tag{21}$$

Replacing for $n_3(t)$ in equation (18) from equation (21), we obtain

$$\dot{m}_3(t) = \frac{C_{se}Q}{n_e}\left[n_3^0 e^{-\lambda_3 t} + \frac{n_2^0\lambda_2}{\lambda_3-\lambda_2}\{e^{-\lambda_2 t} - e^{-\lambda_3 t}\} + \frac{n_1^0\lambda_1\lambda_2}{(\lambda_2-\lambda_1)(\lambda_3-\lambda_1)}\{e^{-\lambda_1 t} - e^{-\lambda_3 t}\}\right.$$

$$\left. - \frac{n_1^0\lambda_1\lambda_2}{(\lambda_2-\lambda_1)(\lambda_3-\lambda_2)}\{e^{-\lambda_2 t} - e^{-\lambda_3 t}\}\right], \qquad t_2 \le t \le t_3 \tag{22}$$

To obtain the fractional release rate, we divide equations (9), (16), and (22) by the 1000-year inventory of the 1st, 2nd, and 3rd members, respectively.

3.3 Species Released Congruent with Waste-matrix Alteration

Species in the fuel matrix that are not solubility-limited can be released congruently with the alteration of the waste matrix when it reacts with water, such as conversion of UO_2 in spent fuel to U_3O_8 by oxygenated water, or the conversion of silica in borosilicate glass to a crystalline mineral phase. UO_2 is oxidized to U_3O_7 without any change in its structure, but in a sufficiently oxidizing environment U_3O_7 becomes U_3O_8, which has a different structure and releases other matrix constituents to react with the surrounding water. Thus, alteration here consists of the oxidative dissolution of uranium and the precipitation of new solid phase(s) of uranium at the waste surface.

To analyze this problem, we consider three time intervals: (1) from first entry of water until the container is filled, (2) after the container is filled until the last alteration, and (3) after all uranium or silica in the waste package has been altered. Before the container has filled, we can write a mass balance for the concentration of species in the water inside the container knowing that the rate of change of the species concentration is equal to rate of alteration release less decay. We interpret f_a, the fractional alteration rate of the waste matrix, as a constant rate based on the initial inventory of the altering species, resulting in a constant mass of that species being altered per unit time. We assume the mass of fuel exposed to water is proportional to the volume of water in the container. The volume increases linearly with time until the container is filled. The governing equation is

$$\frac{d}{dt}(V(t)N(t)) = -N(t)V(t)\lambda + f_a M_M^0 \frac{n(t)}{n_M(t)}\frac{V(t)-V_1(t)}{V(t_2)}, \qquad t_1 \le t \le t_2 \tag{23}$$

with the initial condition

$$N(t_1) = 0 \tag{24}$$

where
$V(t)$ is the volume of water in the container as a function of time (L^3),
$V_1(t)$ is the volume of water in contact with waste that has been completely altered (L^3),
$V(t_2)$ is the volume of water in the filled container (L^3),
$N(t)$ is the concentration of a radionactive species in water (M/L^3),
f_a is the fractional alteration rate (1/t),
M_M^0 is the initial inventory of uranium or silica in the waste (M),
$n(t)$ is the concentration of the species in undissolved waste solid (M/L^3),
$n_M(t)$ is the concentration of the matrix (M/L^3),
λ is the decay constant of species (1/t),
t_1 is the time after emplacement when water first enters a failed container (t),
t_2 is the time after emplacement when container is filled and water overflows (t).

We subtract $V_1(t)$ from $V(t)$ to exclude the portion of fuel that has been completely altered. $1/f_a$ is the time for complete alteration if mass altered per unit time is constant and equal to $f_a M_M^0$. We assume $\lambda_M << \lambda$ and $1/\lambda_M << t_3$, where λ_M, λ are the decay constants of the matrix and the species, respectively, and t_3 is the time beyond which no more release to the rock is expected. Because of the decay of the species in the waste and that of the matrix, we get

$$\frac{n(t)}{n_M(t)} = \frac{n^0 e^{-\lambda t}}{n_M^0 e^{-\lambda_M t}}, \qquad t \geq 0 \tag{25}$$

Hence

$$f_a M_M^0 \frac{n(t)}{n_M(t)} = f_a M_M^0 \frac{n^0 e^{-\lambda t}}{n_M^0 e^{-\lambda_M t}}, \qquad t_1 \leq t \leq t_2 \tag{26}$$

Multiplying the numerator and the denominator on the right hand side of (26) by the waste solid volume and neglecting matrix decay, we get

$$f_a M_M^0 \frac{n^0 e^{-\lambda t}}{n_M^0 e^{-\lambda_M t}} = f_a M_M^0 \frac{M^0 e^{-\lambda t}}{M_M^0 e^{-\lambda_M t}} \simeq f_a M^0 e^{-\lambda t}, \qquad t_1 \leq t \leq t_2 \tag{27}$$

where M^0 is the initial inventory of the species. After the container is filled and until completion of the last alteration, the governing equation differs from equation (23), because now the species begins to leave the container and $V(t)$ is equal to $V(t_2)$. Hence

$$\frac{V(t_2)dN(t)}{dt} = -N(t)V(t_2)\lambda - QN(t) + f_a M_M^0 \frac{n(t)}{n_M(t)} \frac{V(t_2) - V_1(t)}{V(t_2)}, \quad t_2 \leq t \leq t_2 + 1/f_a \tag{28}$$

where $t_2 + 1/f_a$ is the time of the last alteration (t).

The initial condition for equation (28) is obtained by solving equation (23) for $N_i(t_2)$. After all waste matrix in the waste package has been altered, the alteration release rate vanishes. Hence

$$V(t_2)\frac{dN(t)}{dt} = -N(t)V(t_2)\lambda - QN(t), \qquad t_2 + 1/f_a \leq t \leq t_3. \tag{29}$$

The initial condition for (29) is obtained from (28). Figure 3 shows a time-line of events.

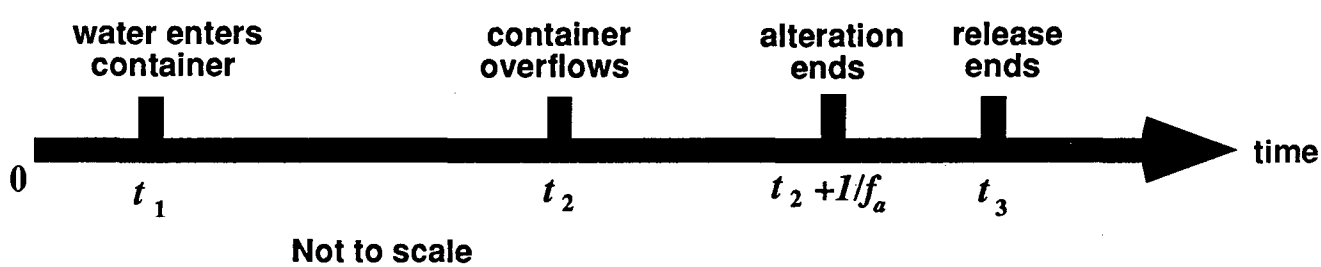

Figure 3. Sequence of Events for Alteration Controlled Wet Drip Contact

We assume that $V_1(t)$ is zero between t_1 and $t_1 + 1/f_a$, the time for alteration to begin, and increases linearly with time until alteration is complete. Assuming the alteration time $1/f_a$ to be less than the container fill time, we get for $V_1(t)$

$$V_1(t) = \begin{cases} 0, & 0 \leq t \leq t_1 + 1/f_a \\ Q(t - t_1 - 1/f_a), & t_1 + 1/f_a < t < t_2 + 1/f_a. \end{cases} \tag{30}$$

Knowing $V(t) = Q(t - t_1)$, $\dfrac{V(t) - V_1(t)}{V(t_2)}$ becomes

$$\frac{V(t)-V_1(t)}{V(t_2)} = \begin{cases} 0, & 0 \le t \le t_1 \\ \frac{Q(t-t_1)}{V(t_2)}, & t_1 \le t \le t_1 + 1/f_a \\ \frac{Q}{V(t_2)f_a}, & t_1 + 1/f_a < t < t_2 \\ \frac{V(t_2)-Q(t-t_1-1/f_a)}{V(t_2)}, & t_2 < t < t_2 + 1/f_a \end{cases} \tag{31}$$

Figures 4 and 5 help clarify equations (30) and (31). We solve (23) by applying the initial condition $N(t_1) = 0$, and we substitute for $\frac{V(t)-V_1(t)}{V(t_2)}$ from equation (31) to obtain the following for the time interval $t_1 \le t \le t_1 + 1/f_a$

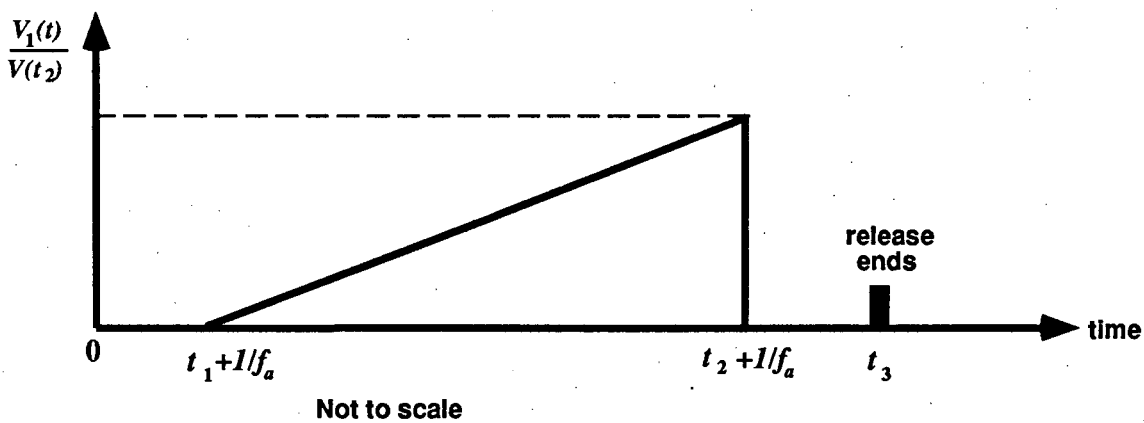

Figure 4. Fraction of Water Volume in Contact with Waste Altered as a Function of Time

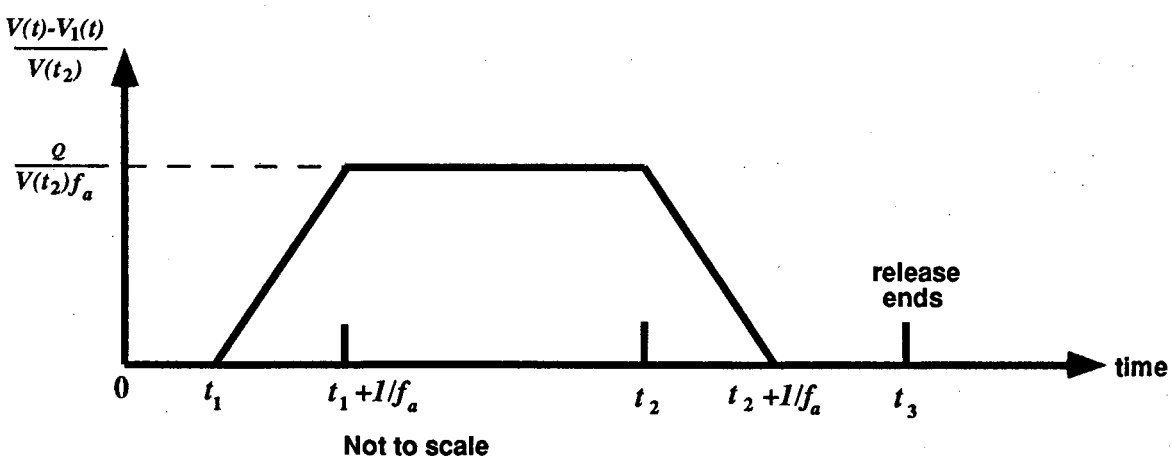

Figure 5. Sequence of Events for Solubility-Limited Wet Drip Contact

$$N(t) = \frac{e^{-\lambda t} f_a M^0}{(t-t_1)V(t_2)} \left[\frac{1}{2}t^2 - t_1 t + \frac{1}{2}t_1^2\right], \qquad t_1 \le t \le t_1 + 1/f_a \tag{32}$$

For the time interval $t_1 + 1/f_a \le t < t_2$, we get

$$N(t) = \frac{e^{-\lambda t} M^0}{V(t_2)(t-t_1)} \left[t - t_1 - \frac{1}{f_a}\right] + \frac{M^0}{V(t_2)(t-t_1)} \left(\frac{1}{2f_a}\right) e^{-\lambda t}, \quad t_1 + 1/f_a \le t \le t_2 \tag{33}$$

We now solve (28) and use (33) to obtain the initial condition. The final result is

$$N(t) = e^{-\lambda t - \alpha t} \frac{f_a M^0}{V(t_2)} \left[\left(\frac{1}{\alpha} + t_1 + \frac{1}{f_a}\right)\left(e^{\alpha t} - e^{\alpha t_2}\right) - \alpha\left(\frac{e^{\alpha t}}{\alpha^2}(\alpha t - 1) - \frac{e^{\alpha t_2}}{\alpha^2}(\alpha t_2 - 1)\right)\right]$$

$$+ \frac{e^{-\lambda t_2} M^0}{V(t_2)(t_2 - t_1)} \left(t_2 - t_1 - \frac{1}{2f_a}\right) e^{(-\lambda-\alpha)(t-t_2)}, \qquad t_2 \le t \le t_2 + 1/f_a \tag{34}$$

where

$$\alpha = Q/V(t_2) \tag{35}$$

Now, to get mass release rate into the rock, we multiply $N(t)$ in (34) by Q

$$\dot{m}(t) = \alpha e^{-\lambda t - \alpha t} f_a M^0 \left[\left(\frac{1}{\alpha} + t_1 + \frac{1}{f_a}\right)\left(e^{\alpha t} - e^{\alpha t_2}\right) - \alpha\left(\frac{e^{\alpha t}}{\alpha^2}(\alpha t - 1) - \frac{e^{\alpha t_2}}{\alpha^2}(\alpha t_2 - 1)\right)\right]$$

$$+ \alpha \frac{e^{-\lambda t_2} M^0}{(t_2 - t_1)} \left(t_2 - t_1 - \frac{1}{2f_a}\right) e^{(-\lambda-\alpha)(t-t_2)}, \qquad t_2 \le t \le t_2 + 1/f_a \tag{36}$$

The fractional release rate is obtained by dividing $\dot{m}(t)$ by $M^\star$

$$f(t) = \frac{\dot{m}(t)}{M^\star} \tag{37}$$

Now we solve equation (29) in the time interval $t_2 + 1/f_a \le t \le t_3$. The initial condition for (29) is obtained by replacing $t_2 + 1/f_a$ for t in equation (34). The solution is

$$N(t) = c_4 e^{(-\lambda-\alpha)(t-t_2-1/f_a)}, \qquad t_2 + 1/f_a \le t \le t_3 \tag{38}$$

c_4 is obtained from applying the initial condition. Therefore

$$N(t) = \left\{ e^{(-\lambda-\alpha)(t_2+1/f_a)} \frac{f_a M^0}{V(t_2)} \left[\left(\frac{1}{\alpha} + t_1 + \frac{1}{f_a}\right)\left(e^{\alpha(t_2+1/f_a)} - e^{\alpha t_2}\right)\right.\right.$$

$$\left. - \alpha\left(\frac{e^{\alpha(t_2+1/f_a)}}{\alpha^2}\left[\alpha t_2 + \frac{\alpha}{f_a} - 1\right] - \frac{e^{\alpha t_2}}{\alpha^2}(\alpha t_2 - 1)\right)\right]$$

$$\left. + \frac{e^{-\lambda t_2} M^0}{V(t_2)(t_2 - t_1)} \left(t_2 - t_1 - \frac{1}{2f_a}\right) e^{(-\lambda-\alpha)(1/f_a)} \right\} e^{(-\lambda-\alpha)(t-t_2-1/f_a)}, \qquad t_2 + 1/f_a \le t \le t_3 \tag{39}$$

From which we get the mass release rate as

$$\dot{m}(t) = \alpha\Bigg\{e^{(-\lambda-\alpha)(t_2+1/f_a)} f_a M^0 \Bigg[\left(\frac{1}{\alpha} + t_1 + \frac{1}{f_a}\right)\left(e^{\alpha(t_2+1/f_a)} - e^{\alpha t_2}\right)$$

$$-\alpha\left(\frac{e^{\alpha(t_2+1/f_a)}}{\alpha^2}\left[\alpha t_2 + \frac{\alpha}{f_a} - 1\right] - \frac{e^{\alpha t_2}}{\alpha^2}(\alpha t_2 - 1)\right)\Bigg]$$

$$+\frac{e^{-\lambda t_2} M^0}{(t_2 - t_1)}\left(t_2 - t_1 - \frac{1}{2f_a}\right) e^{(-\lambda-\alpha)(1/f_a)}\Bigg\} e^{(-\lambda-\alpha)(t-t_2-1/f_a)}, \quad t_2 + 1/f_a \le t \le t_3 \tag{40}$$

and the fractional release rate is

$$f(t) = \frac{\dot{m}(t)}{M^\star} \tag{41}$$

At $t = t_2 + 1/f_a$, we get

$$N(t_2 + 1/f_a) = c_4 = e^{(-\lambda-\alpha)(t_2+1/f_a)} \frac{f_a M^0}{V(t_2)}\Bigg[\left(\frac{1}{\alpha} + t_1 + \frac{1}{f_a}\right)\left(e^{\alpha(t_2+1/f_a)} - e^{\alpha t_2}\right)$$

$$-\alpha\left(\frac{e^{\alpha(t_2+1/f_a)}}{\alpha^2}(\alpha t_2 + \alpha/f_a - 1) - \frac{e^{\alpha t_2}}{\alpha^2}(\alpha t_2 - 1)\right)\Bigg] + \frac{e^{-\lambda t_2} M^0}{V(t_2)(t_2 - t_1)}\left(t_2 - t_1 - \frac{1}{f_a}\right) e^{(-\lambda-\alpha)(1/f_a)} \tag{42}$$

and

$$\dot{m}(t_2 + 1/f_a) = \alpha e^{(-\lambda-\alpha)(t_2+1/f_a)} f_a M^0 \Bigg[\left(\frac{1}{\alpha} + t_1 + \frac{1}{f_a}\right)\left(e^{\alpha(t_2+1/f_a)} - e^{\alpha t_2}\right)$$

$$-\alpha\left(\frac{e^{\alpha(t_2+1/f_a)}}{\alpha^2}(\alpha t_2 + \alpha/f_a - 1) - \frac{e^{\alpha t_2}}{\alpha^2}(\alpha t_2 - 1)\right)\Bigg] + \alpha\frac{e^{-\lambda t_2} M^0}{(t_2 - t_1)}\left(t_2 - t_1 - \frac{1}{2f_a}\right) e^{(-\lambda-\alpha)(1/f_a)} \tag{43}$$

We can solve for t_3, the time after emplacement beyond which no more release to the rock is expected, by setting $\dot{m}(t)$ in equation (40) equal to zero and substituting t_3 for t. Hence

$$QN(t_2 + 1/f_a) e^{(-\lambda-\alpha)(t_3-t_2-1/f_a)} = 0 \tag{44}$$

which means

$$e^{(-\lambda-\alpha)(t_3-t_2-1/f_a)} = 0 \tag{45}$$

Equation (45) means t_3 must be infinitely large for the equation to hold; therefore, $t_3 = \infty$.

If the time for alteration to be completed, $1/f_a$, is much larger than the container fill time, (23), (28) and (29) are still valid. However, we now have

$$V_1(t) = 0, \qquad 0 \le t \le t_2 + 1/f_a \tag{46}$$

Hence

$$\frac{V(t) - V_1(t)}{V(t_2)} = \begin{cases} \frac{Q(t-t_1)}{V(t_2)}, & t_1 \le t \le t_2 \\ 1, & t_2 \le t \le t_2 + 1/f_a \end{cases} \tag{47}$$

The solution for the time period $t_2 \leq t \leq t_2 + 1/f_a$ is

$$\dot{m} = f_a M^o e^{-(\alpha+\lambda)t} \left[(e^{\alpha t} - e^{\alpha t_2}) + \frac{\alpha^2}{2}(t_2 - t_1)^2 e^{\alpha t_2} \right], \quad t_2 \leq t \leq t_2 + 1/f_a \tag{48}$$

In the period $t_2 + 1/f_a \leq t \leq t_3$ the solution is

$$\dot{m} = f_a M^o e^{-(\alpha+\lambda)t} \left[(e^{\alpha(t_2+1/f_a)} - e^{\alpha t_2}) + \frac{\alpha^2}{2}(t_2 - t_1)^2 e^{\alpha t_2} \right], \quad t_2 + 1/f_a \leq t \leq t_3 \tag{49}$$

from which the fractional release rates can be calculated by $f(t) = \dot{m}(t)/M^\star$.

3.4 Readily Soluble Species

In a spent fuel waste package soluble cesium and iodine accumulate in fuel-cladding gaps, voids, amd grain boundaries. Such readily soluble species are known to dissolve rapidly when contacted by water. Assuming instant dissolution of the readily soluble species, we write a governing equation by noting that the rate of change of species concentration multiplied by the volume of water in the filled container $V(t_2)$ is equal to mass coming in minus mass going out minus the decay term. At t_2, the soluble species concentration is N_0. N_0 is obtained by taking the fraction of species inventory that is readily soluble at time t_2 and dividing it by the volume of water in the filled container $V(t_2)$. At times greater than t_2, no more dissolution occurs. Hence the equation is

$$V(t_2)\frac{dN(t)}{dt} = -QN(t) - N(t)V(t_2)\lambda, \qquad t_2 \leq t \leq t_3' \tag{50}$$

with the initial condition

$$N(t_2) = N_0 = \frac{wM^0 e^{-\lambda t_2}}{V(t_2)} \tag{51}$$

where
$N(t)$ is the concentration of species in volume $V(t_2)$ at t (M/L^3),
w is the fraction of the inventory that is readily soluble,
M^0 is the species initial inventory (M),
t_2 is the fill time after emplacement (t),
t_3' is the time beyond which no more release to the rock is expected (t).

The solution to equation (46) is

$$N(t) = \frac{wM^0 e^{-\lambda t_2}}{V(t_2)} e^{-(\alpha+\lambda)(t-t_2)}, \qquad t_2 \leq t \leq t_3' \tag{52}$$

The mass release rate into the rock is obtained by multiplying $N(t)$ by Q

$$\dot{m}(t) = \alpha w M^0 e^{-\lambda t_2} e^{-(\alpha+\lambda)(t-t_2)}, \qquad t_2 \leq t \leq t_3' \tag{53}$$

The fractional release rate is

$$f(t) = \alpha \frac{wM^0 e^{-\lambda t_2}}{M^\star} e^{-(\alpha+\lambda)(t-t_2)}, \qquad t_2 \leq t \leq t_3' \tag{54}$$

4. EQUATIONS FOR THE MOIST-CONTINUOUS WATER-CONTACT MODE

We present analytic equations for the release of three types of radioactive species. Figure 6 is a sketch of a waste package in the moist-continuous contact mode.

4.1 Solubility-Limited Release

The time-dependent fractional release rate of a low-solubility species from an equivalent spherical waste can be estimated from the equations by Chambré *et al.* [1990] for release from waste directly into rock and by equations given by Chambré *et al.* [1985] for release into rock through a backfill. We assume that mass transfer occurs by molecular diffusion because the expected ground-water velocities are low. Decay within the waste solid is neglected.

4.1.1 Solubility-limited Release from the Waste Directly into Tuff

Here we consider the release of solubility-limited species in an unsaturated repository, if a significant portion of the degraded container is in contact with surrounding intact rock. The analysis is also applicable for a saturated repository, if the original gap is filled with water making the solubility at the waste surface and at the inner surface of the rock the same because of the well-mixed water in the gap. The governing equation, for a waste sphere of equal surface area, for the radionuclide concentration $N(r,t)$ for release from the waste directly into rock is

$$K\frac{\partial N(r,t)}{\partial t} = \sigma D_f \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial N(r,t)}{\partial r}\right) - \lambda K N, \qquad r > R_0, t > 0 \tag{55}$$

where
K is the retardation coefficient of species, dimensionless,
R_0 is the radius of an equivalent-area waste sphere (L),
D_f is the diffusion coefficient in a water continuum (L^2/t),
σ is the tortousity of intact tuff.

The inventory fraction of the isotope is γ, assumed to be a constant and equal to $M^\star/M_e^\star$, where $M^\star$ is the 1000-year inventory of the isotope and $M_e^\star$ is the 1000-year inventory of the element. The isotopic fraction γ is actually time-dependent, but if we assume all the isotopes have negligible decay, we can use a constant γ.

The initial condition is

$$N(r,0) = 0, \qquad r > R_0 \tag{56}$$

The boundary conditions are

$$N(R_0,t) = C_{se}\gamma, \qquad t \geq 0 \tag{57}$$

$$N(\infty,t) = 0, \qquad t \geq 0 \tag{58}$$

Assuming that local chemical equilibrium exists between a species in the pore liquid and that same species sorbed in the rock, K is given by

$$K = 1 + \frac{1-\epsilon}{\epsilon\psi}\rho K_d \tag{59}$$

where K_d is the sorption ratio (activity of radionuclide on solid phase per unit mass of solid divided by activity of radionuclide in solution per unit volume of solutions), ϵ is the rock-matrix porosity, ψ is the saturation fraction, and ρ is the crushed-tuff density.

The details of the solution to (55) through (58), for $\psi = 1$, is given in Chambré *et al.* [1990]. The total mass transfer rate from the waste form surface into the surrounding porous rock is

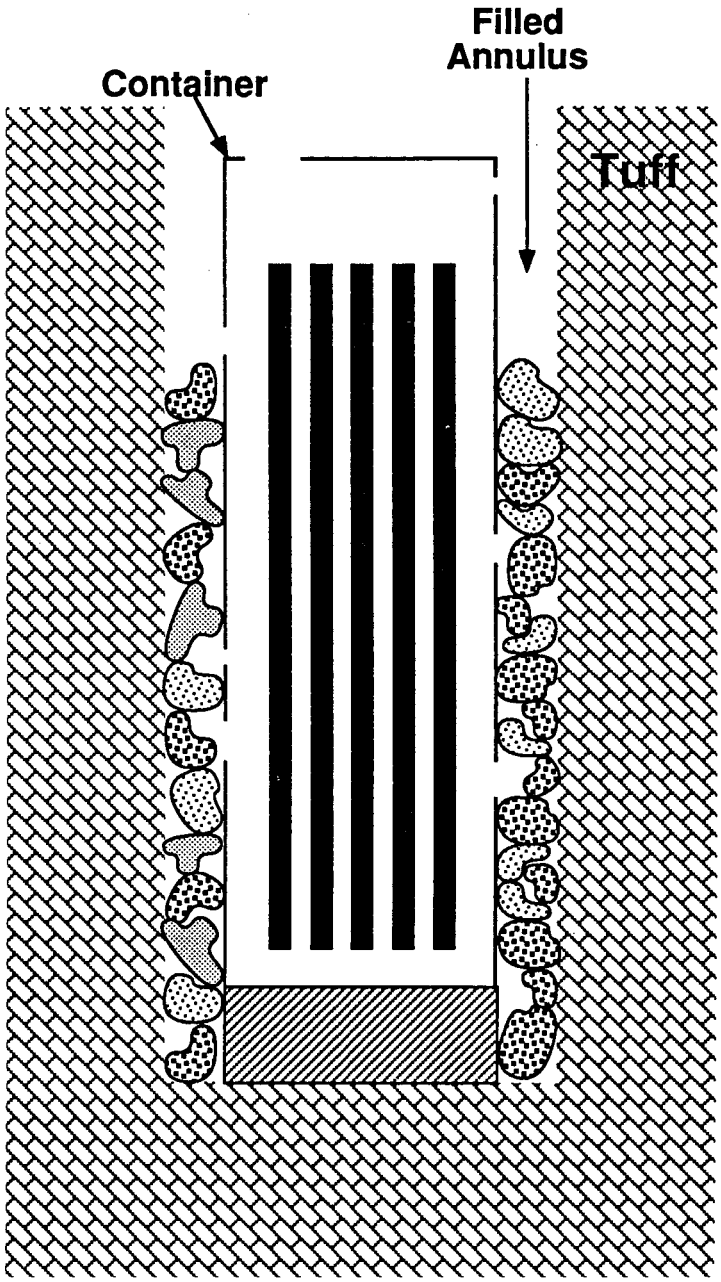

Figure 6. The Moist-continuous Water Contact Mode

$$\dot{m}(t) = -4\pi R_0^2 \epsilon\psi\sigma D_f \frac{\partial N(r,t)}{\partial r}\bigg|_{r=R_0}, \qquad t > 0 \tag{60}$$

where $\epsilon\psi$ is the rock effective porosity.

$\dot{m}(t)$ is obtained by first solving (55) for $N(r,t)$ subject to the side conditions, differentiating $N(r,t)$ with respect to r for r equal to R_0, and finally evaluating $\frac{\partial N(R_0,t)}{\partial r}$ in (60). The fractional release rate $f(t)$, normalized to the 1000-year inventory, is given by

$$f(t) = \frac{\dot{m}(t)}{M^\star} = \frac{4\pi R_0 C_{se}\gamma\sigma D_f \epsilon\psi}{M^\star}\left\{1 + \sqrt{\frac{K\lambda R_0^2}{D_f}}\mathrm{erf}(\sqrt{\lambda t}) + \sqrt{\frac{K R_0^2}{\pi D_f t}}e^{-\lambda t}\right\}, \qquad t > 0 \tag{61}$$

For a saturated repository, ψ will be unity.

4.1.2 Solubility-limited Release into Tuff Through a Filled Annulus

If the annulus becomes filled with rubble and fines, we can treat this annulus of thickness $b = R_1 - R_0$ as a backfill. For an unsaturated repository and a saturated repository, the governing equations in the backfill (subscript 1) and rock (subscript 2) regions for a radionuclide without any precursor in equivalent spherical geometry are given by

$$\frac{\partial N_1(r,t)}{\partial t} = D_1 \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial N_1(r,t)}{\partial r}\right) - \lambda N_1, \qquad R_0 < r < R_1, \quad t > 0 \tag{62}$$

$$\frac{\partial N_2(r,t)}{\partial t} = D_2 \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial N_2(r,t)}{\partial r}\right) - \lambda N_2, \qquad R_1 < r < \infty, \quad t > 0 \tag{63}$$

with

$$D_1 = \frac{\sigma_1 D_f}{K_1} \qquad D_2 = \frac{\sigma_2 D_f}{K_2} \tag{64}$$

The initial conditions are

$$N_1(r,0) = 0, \qquad R_0 < r \leq R_1 \tag{64}$$

$$N_2(r,0) = 0, \qquad R_1 \leq r < \infty. \tag{66}$$

The boundary conditions are given by

$$N_1(R_0,t) = C_{se}\gamma, \qquad t \geq 0 \tag{67}$$

$$N_2(\infty,t) = 0, \qquad t \geq 0 \tag{68}$$

$$-\epsilon_1\psi_1 D_f \sigma_1 \frac{\partial N_1}{\partial r} = -\epsilon_2\psi_2 D_f \sigma_2 \frac{\partial N_2}{\partial r} \qquad \text{at} \quad R_1, \qquad t \geq 0 \tag{69}$$

$$N_1(R_1,t) = N_2(R_1,t), \qquad t \geq 0. \tag{70}$$

In the above equations subscript 1 is for the annulus/backfill, subscript 2 is for the tuff/rock, ψ_i is the saturation fraction, $\epsilon_1\psi_1$ is the effective porosity in the filled annulus and is given by

$$\epsilon_1\psi_1 = (1 - \epsilon_b)\epsilon\psi_1 \tag{71}$$

where

ϵ is the porosity of the tuff,
ϵ_b is the volume of air between rubble pieces divided by the total bed volume,

In intact tuff the effective porosity is

$$\epsilon_2\psi_2 = \epsilon\psi_2 \tag{72}$$

Here K_i is the retardation coefficient, σ_1 is the tortuosity in the annulus/backfill consisting of: tortuosity due to tortuous diffusion pathways within a rubble piece and that of the contact areas between rubble pieces. The tortuosity of the contact areas is discussed in a separate report [Sadeghi *et al.* 1990b] σ_2 is the tortuosity in the intact tuff, and R_0 is the radius of an equivalent-area waste sphere (L).

The details of the solution method are given in Chambré *et al.* [1985]. We give below the time-dependent species concentrations and fluxes. The backfill thickness is $b = R_1 - R_0$, where R_1 is the radius of the outer edge of the backfill shell. The equation for $N_1(r,t)$, the species concentration in the backfill, is

$$\frac{N_1(r,t)}{C_{se}\gamma} = \frac{N_1(r,\infty)}{C_{se}\gamma} + e^{-\lambda t}\int_0^\infty \frac{e^{-D_1 t\eta^2}}{1+\left(\frac{\lambda}{D_1\eta^2}\right)} I(r,\eta)d\eta, \qquad R_0 \le r \le R_1, t \ge 0 \tag{73}$$

where

$$\frac{N_1(r,\infty)}{C_{se}\gamma} = \frac{R_0}{r}\left\{\frac{\epsilon_1'\mu_1\cosh\mu_1(R_1-r) + (\epsilon_2'\mu_2+\Gamma)\sinh\mu_1(R_1-r)}{\epsilon_1'\mu_1\cosh(\mu_1 b) + (\epsilon_2'\mu_2+\Gamma)\sinh(\mu_1 b)}\right\}$$

$$I(r,\eta) = -\left(\frac{2R_0\epsilon_1'\epsilon_2'\beta}{\pi r}\right)\frac{\eta\sin(\eta[r-R_0])}{H(\eta)}, \qquad \beta = \sqrt{K_2'/K_1'}$$

$$H(\eta) = \left[\epsilon_1'\eta\cos(\eta b) + \frac{\epsilon_2'-\epsilon_1'}{R_1}\sin(\eta b)\right]^2 + [\beta\epsilon_2'\eta\sin(\eta b)]^2, \qquad \Gamma = \frac{\epsilon_2'-\epsilon_1'}{R_1}$$

$$\mu_\ell = \sqrt{\frac{\lambda}{D_\ell}}, \qquad K_\ell' = K_\ell/\sigma_\ell, \qquad \epsilon_\ell' = \epsilon_\ell\sigma_\ell\psi_\ell, \qquad \ell = 1,2 \tag{74}$$

The total mass transfer rate at any location in the backfill is obtained by

$$\dot{m}(r,t) = -4\pi r^2\epsilon_1\psi_1\sigma_1 D_f\frac{\partial N_1(r,t)}{\partial r}, \qquad R_0 \le r \le R_1, t \ge 0 \tag{75}$$

which is

$$\frac{\dot{m}(r,t)}{C_{se}\gamma} = 4\pi\epsilon_1\psi_1\sigma_1 D_f R_0 r\left\{\frac{(\frac{1}{r})(\epsilon_1'\mu_1\cosh\mu_1(R_1-r) + (\epsilon_2'\mu_2+\Gamma)\sinh\mu_1(R_1-r))}{\epsilon_1'\mu_1\cosh(\mu_1 b) + (\epsilon_2'\mu_2+\Gamma)\sinh(\mu_1 b)}\right.$$

$$\frac{-(-\epsilon_1'\mu_1^2\sinh\mu_1(R_1-r) - \mu_1(\epsilon_2'\mu_2+\Gamma)\cosh\mu_1(R_1-r))}{\epsilon_1'\mu_1\cosh(\mu_1 b) + (\epsilon_2'\mu_2+\Gamma)\sinh(\mu_1 b)}$$

$$\left. + \frac{2\epsilon_1'\epsilon_2'\beta}{\pi}e^{-\lambda t}\int_0^\infty \frac{e^{-D_1 t\eta^2}}{1+(\frac{\lambda}{D_1\eta^2})}\frac{\eta[\eta\cos(\eta[r-R_0]) - \frac{1}{r}\sin(\eta[r-R_0])]}{H(\eta)}d\eta\right\}, \qquad R_0 \le r \le R_1, \quad t \ge 0 \tag{76}$$

For a saturated repository, ψ_1 and ψ_2 are unity.

4.2 Readily Soluble Species

For release of readily soluble species from the fuel-cladding gap, plenum, and grain boundaries, we adopt analytic solutions in Chambré *et al.* [1990] for equivalent planar geometry, with equal diffusion coefficients in the backfill and rock. The origin of the x axis is at the annulus/tuff interface, and $-b$ is the annulus

thickness. Here we generalize that result to the case of unequal diffusion coefficients in the filled annular layer and intact rock. The governing equations in the filled annular layer and intact tuff regions are

$$\frac{\partial N_1}{\partial t} = D_1 \frac{\partial^2 N_1}{\partial x^2} - \lambda N_1, \qquad -b < x < 0, \quad t > 0 \tag{77}$$

$$\frac{\partial N_2}{\partial t} = D_2 \frac{\partial^2 N_2}{\partial x^2} - \lambda N_2, \qquad x > 0, \quad t > 0 \tag{78}$$

with

$$D_1 = \frac{\sigma_1 D_f}{K_1} \qquad\qquad D_2 = \frac{\sigma_2 D_f}{K_2}. \tag{79}$$

The initial and boundary conditions are

$$N_1(x,0) = 0, \qquad -b < x < 0 \tag{80}$$

$$N_2(x,0) = 0, \qquad x > 0 \tag{81}$$

$$N_1(0,t) = N_2(0,t), \qquad t > 0 \tag{82}$$

$$-\epsilon_1 \psi_1 D_f \sigma_1 \frac{\partial N_1}{\partial x} = -\epsilon_2 \psi_2 D_f \sigma_2 \frac{\partial N_2}{\partial x} \qquad \text{at} \quad x = 0, \qquad t > 0 \tag{83}$$

$$N_2(\infty,t) = 0, \qquad t > 0. \tag{84}$$

where
b is the annulus thickness (L),
ψ_i is the saturation fraction,
$\epsilon_1\psi_1$ is the effective porosity in the filled annulus,
$\epsilon_2\psi_2$ is the effective porosity in the intact tuff,
K_i are the retardation coefficients,
D_f is the species diffusion coefficient in a water continuum (L^2/t),
S is the surface area at the waste-backfill interface, assumed to be equal to the surface area of the waste cylinder (L^2),
σ_i are tortousity correction factors,
V is the volume of void space in the waste container (for spent fuel it includes the empty space in the container not occupied by the spent-fuel rods or assemblies),
N^0 is the initial species concentration in the void space, after the void space is filled with water.
For a saturated repository, ψ_1 and ψ_2 are unity.

The retardation coefficients K_1 and K_2 are given by (59); $\epsilon_1\psi_1$ and $\epsilon_2\psi_2$ are obtained from (71) and (72) respectively. A mass balance within the water-filled region inside the waste package is

$$-V \frac{\partial N_1(-b,t)}{\partial t} = -D_f \sigma_1 \epsilon_1 \psi_1 S \frac{\partial N_1(-b,t)}{\partial x} + \lambda V N_1(-b,t), \qquad t > 0 \tag{85}$$

The initial concentration is

$$N_1(-b,0) = N^0 \qquad \text{known} \tag{86}$$

The total mass transfer rate of the radionuclide at the outer wall of the annulus is

$$\dot{m}(0,t) = -D_f \sigma_1 \epsilon_1 \psi_1 S \frac{\partial N_1(0,t)}{\partial x}, \tag{87}$$

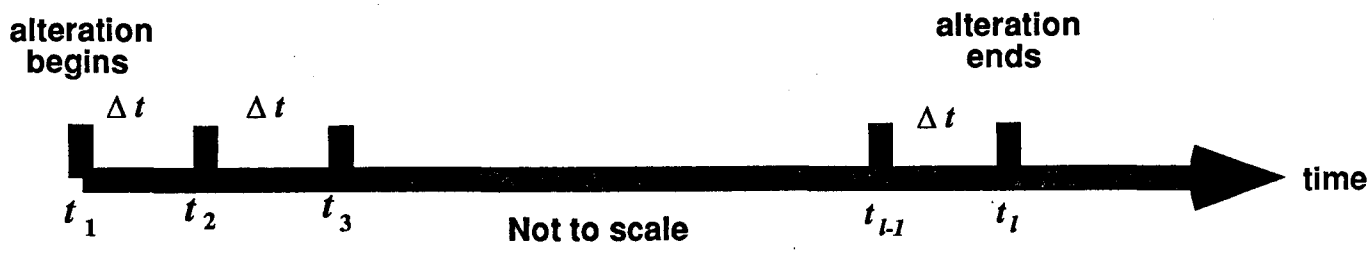

Figure 7. Equal Interval Input of Species Released Congruent with Matrix Alteration

which is equivalent to

$$\dot{m}(0,t) = 2K_1\epsilon_1\psi_1 N^\circ S\frac{e^{-\lambda t}}{(\delta+1)}\sum_{n=0}^{\infty}\left\{\left[\sqrt{\frac{D_1}{\pi t}} - \Omega_0 D_1 \mathrm{F}(\phi_n^2)\right]\exp\left[\frac{-(2n+1)^2b^2}{4D_1 t}\right]\right\}\left(\frac{\delta-1}{\delta+1}\right)^n, \quad t \geq 0 \quad (88)$$

where

$$\mathrm{F}(z^2) = \exp\{z^2\}\mathrm{erfc}(z), \qquad \phi_n = \frac{(2n+1)b}{2\sqrt{D_1 t}} + \Omega_0\sqrt{D_1 t}$$

$$\delta = \frac{\epsilon_1\psi_1}{\epsilon_2\psi_2}\sqrt{\frac{K_1\sigma_1}{K_2\sigma_2}}, \qquad \Omega_0 = K_1\epsilon_1\psi_1\frac{S}{V} \quad (89)$$

4.3 Species Released Congruent with Waste-matrix Alteration

For alteration-controlled diffusive release we adopt equations given in Section 4.2 for the release of readily soluble species to obtain an approximate numerical solution. Assuming the mass altered per unit time is constant and equal to $f_a M_M^0$, where f_a is the fractional alteration rate (1/t) and M_M^0 is the initial inventory of the waste matrix (M), the species mass release rate into the water-filled region inside the waste package, $\dot{m}_M$, is given by equation (27)

$$\dot{m}_M = f_a M_M^0 \frac{n^0 e^{-\lambda t}}{n_M^0 e^{-\lambda_M t}} = f_a M_M^0 \frac{M^0 e^{-\lambda t}}{M_M^0 e^{-\lambda_M t}} = f_a M^0 e^{-t(\lambda-\lambda_M)}, \qquad t_1 \leq t \leq t_\ell \quad (90)$$

where
t_1 is the time when water contacts the waste and alteration begins (t),
t_ℓ is the time when alteration is complete (t),
M^0 is the initial inventory of the species (M),
M_M^0 is the initial inventory of the matrix (M),
$n(t)$ is the concentration of the species in the undissolved solid (M/L^3),
$n_M(t)$ is the concentration of matrix (M/L^3).

We divide the time $t_\ell - t_1$ into intervals, calculate the species inventory released into the container water for each interval, and convert the inventory to a concentration increment. For sufficiently small time intervals of release into the container water, we can apply the equations in Section 4.2 to obtain the contributions to the time-dependent release rate into surrounding rock from dissolution into a given time increment. The total mass release rate is the sum of all the mass release rates obtained for each time interval. Figure 7 shows the calculation concept.

In each time interval we calculate the amount of the matrix that would be altered and instantaneously dissolve that amount at the beginning of that time interval. This amount results in a certain concentration increment.

$$\Delta N_1(-b,t_1) = \frac{f_a M^0 \Delta t}{V} e^{-t_1(\lambda-\lambda_M)}$$

$$\Delta N_2(-b,t_2) = \frac{f_a M^0 \Delta t}{V} e^{-t_2(\lambda-\lambda_M)}$$

$$\vdots$$

$$\Delta N_{\ell-1}(-b,t_{\ell-1}) = \frac{f_a M^0 \Delta t}{V} e^{-t_{\ell-1}(\lambda-\lambda_M)} \tag{91}$$

where
V is the void volume (L^3),
Δt is the time interval (t).

Using (88), the mass release rate at the annular wall due to the mass released in the first interval is

$$\Delta\dot{m}_1(0,t) = 2K_1\epsilon_1\psi_1 \left(\frac{f_a M^0 \Delta t e^{-t_1(\lambda-\lambda_M)}}{V}\right) S\frac{e^{-\lambda(t-t_1)}}{(\delta+1)}$$

$$\times \sum_{n=0}^{\infty}\left\{\left[\sqrt{\frac{D_1}{\pi(t-t_1)}} - \Omega_0 D_1 \mathrm{F}(\phi_n^2)\right]\exp\left[\frac{-(2n+1)^2b^2}{4D_1(t-t_1)}\right]\right\}\left(\frac{\delta-1}{\delta+1}\right)^n, \qquad t \geq t_1 \tag{92}$$

Similarly the mass release rate due to the mass released in the second interval is

$$\Delta\dot{m}_2(0,t) = 2K_1\epsilon_1\psi_1 \left(\frac{f_a M^0 \Delta t e^{-t_2(\lambda-\lambda_M)}}{V}\right) S\frac{e^{-\lambda(t-t_2)}}{(\delta+1)}$$

$$\times \sum_{n=0}^{\infty}\left\{\left[\sqrt{\frac{D_1}{\pi(t-t_2)}} - \Omega_0 D_1 \mathrm{F}(\phi_n^2)\right]\exp\left[\frac{-(2n+1)^2b^2}{4D_1(t-t_2)}\right]\right\}\left(\frac{\delta-1}{\delta+1}\right)^n, \qquad t \geq t_2 \tag{93}$$

and so on. For the last interval, we obtain

$$\Delta\dot{m}_{\ell-1}(0,t) = 2K_1\epsilon_1\psi_1 \left(\frac{f_a M^0 \Delta t e^{-t_{\ell-1}(\lambda-\lambda_M)}}{V}\right) S\frac{e^{-\lambda(t-t_{\ell-1})}}{(\delta+1)}$$

$$\times \sum_{n=0}^{\infty}\left\{\left[\sqrt{\frac{D_1}{\pi(t-t_{\ell-1})}} - \Omega_0 D_1 \mathrm{F}(\phi_n^2)\right]\exp\left[\frac{-(2n+1)^2b^2}{4D_1(t-t_{\ell-1})}\right]\right\}\left(\frac{\delta-1}{\delta+1}\right)^n, \qquad t \geq t_\ell \tag{94}$$

Now we invoke the principle of superposition and add all the mass release rates $\Delta\dot{m}_1, \ldots, \Delta\dot{m}_{\ell-1}$ to obtain the total mass release rate $\dot{m}(0,t)$ at the outer wall of the annulus. Hence

$$\dot{m}(0,t) = \sum_{i=1}^{\ell-1} \Delta\dot{m}_i(0,t), \qquad t \geq t_1 \tag{91}$$

The fractional release rate $f(t)$, normalized to the 1000-year inventory, can be calculated by dividing $\dot{m}(0,t)$ by $M^\star$.

5. Conclusion

Analytic equations have been given for calculating release rates from waste packages in a nuclear waste repository in partially saturated rock. Two water contact modes have been considered—wet-drip and moist-continuous. The solutions given cover species that are solubility-limited, readily soluble, and those whose releases are congruent with waste matrix alteration. Numerical illustrations of these equations appear in a separate report [Sadeghi *et al.* 1990a].

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NOMENCLATURE

$b = R_1 - R_0$ is the backfill/annulus thickness (L),
C_{se} is the elemental solubility (M/L^3),
f_a, the fractional alteration rate of the waste matrix (1/t),
$f_i(t)$ is the fractional release rate of the isotope (1/t),
M_i^0 is the initial inventory of the isotope (M),
M_M^0 is the initial inventory of uranium or silica in the waste (M),
$M_i^\star$ is the 1000-year inventory of the isotope (M),
$\dot{m}_i(t)$ is the mass release rate of the species (M/t),
$N(t)$ is the concentration of a radionactive species in water (M/L^3),
$n_i(t)$ is the concentration of the species in the undissolved solid (M/L^3),
$n_e(t)$ is the concentration of the element in the undissolved solid (M/L^3),
$n_M(t)$ is the concentration of the matrix (M/L^3),
N_0 is the initial soluble species concentration (M/L^3),
Q is the volumetric flow rate of water into and out of the container (L^3/t),
R_0 is the radius of an equivalent-area waste sphere (L),
R_1 is the radius of the outer edge of the backfill shell (L),
S is the surface area at the waste-backfill interface, or the surface area of the waste cylinder (L^2),
Δt is a time interval (t),
t_1 is when water first enters the failed container (t),
t_2 is the time after emplacement when the container is full of water (t),
t_3 is when all of the element has dissolved (t),
t_ℓ is the time when alteration is complete (t),
V is the volume of void space in the waste container (L^2),
$V(t)$ is the volume of water in the container as a function of time (L^3),
$V_1(t)$ is the volume of water in contact with waste that has been completely altered (L^3),
$V(t_2)$ is the volume of water in the filled container (L^3),
w is the fraction of the inventory that is readily soluble,
ϵ is the porosity of the intact tuff,
ϵ_b is the volume of air between rubble pieces divided by the total bed volume,
$\epsilon_1\psi_1$ is the effective porosity in the filled annulus,
$\epsilon_2\psi_2$ is the effective porosity in tuff,
γ is the inventory fraction of the isotope,
λ is the decay constant of species (1/t),
ρ is the crushed-tuff density (M/L^3),
σ is the tortousity of intact tuff,
ψ is the saturation fraction.

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