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RELEASE RATES OF SOLUBLE SPECIES AT YUCCA MOUNTAIN

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ABSTRACT

Experimental leaching of spent fuel shows that some fission product species are preferentially released upon contact with water. We analyze the conservative case of bare spent fuel in contact with saturated tuff using diffusional mass transfer analysis. For the parameter values used, the USNRC release rate limit is not exceeded, except for ^{99}Tc. The presence of a container and the distribution of water contact over time will assist in meeting this criterion.

INTRODUCTION

To determine compliance with the U. S. Nuclear Regulatory Commission's release rate criterion for the engineered barrier system,[1] the Yucca Mountain project plans to analyse a bounding case which can be described as 'abundant water and bare waste.'[2] In this paper we present a conservative and perhaps bounding analysis of the release rate of readily soluble species.

READILY SOLUBLE SPECIES

When ground water contacts spent fuel at a high-level waste repository, release of radioactive species will begin. This release is a series of complex processes. First, soluble fission products like cesium and iodine, which have accumulated in fuel/shealth gap and voids and cracks in the spent fuel will release rapidly. This is accompanied by a gradual but continued preferential leaching of the same species from grain boundaries. At the same time, there is slower release of species due to the dissolution of UO$_2$ grains.[3] For several years we have advocated that the slow release of species related to UO$_2$ can be studied as solubility-limited dissolution.[4,5] The first two, more rapid processes can be studied as mass-transfer-limited transport.[6] In this paper we apply the latter analysis to Yucca Mountain.

We refer to species such as ^{135}Cs, ^{129}I and ^{99}Tc in spent fuel as the instant-release fraction[7] or soluble species. Garisto et al.[7] estimated the instant-release fraction of ^{135}Cs and ^{129}I to be normally distributed with a mean of 8.1% and a standard deviation of 0.6%. They also estimated the instant-release fraction of ^{99}Tc to be normally distributed with a mean of 6.0% and a standard deviation of 0.6%.

ANALYSIS

We assume that upon contact with ground water there is instantaneous dissolution of the soluble species into a volume V of ground water that has penetrated in the waste package voids at failure time, and that advection is low enough that mass-transfer into surrounding porous rock is controlled by molecular diffusion. We assume that the surrounding porous rock is in direct contact with the well-mixed void liquid (Figure 1a), that contains initially a specified quantity of these readily soluble species. Linear geometry is used in analyzing the dissolution of readily soluble species. The species migrate into the porous material under a concentration gradient. Assuming that advective transport in the near-field is small compared with diffusive transport, the mass balance for $c(x,t)$, the space-time-dependent concentration in pore water, is

$$K \frac{\partial c(x,t)}{\partial t} = D \frac{\partial^2 c(x,t)}{\partial x^2} - \lambda K c(x,t), \quad x > a, \quad t > 0$$
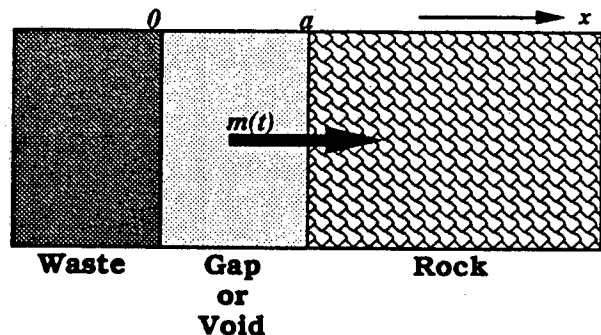
(1)

Figure 1a. Release of Soluble Species into Rock

where D is the species diffusion coefficient in the porous rock [L^2/t]
K is the species retardation coefficient,
λ is the species decay constant [t^{-1}].

The initial and boundary conditions are

$$c(x,0) = 0, \qquad x > a \qquad (2)$$

$$c(a,t) = \eta(t), \qquad t \geq 0 \qquad (3)$$

$$c(\infty,t) = 0, \qquad t \geq 0 \qquad (4)$$

where a is the thickness of the "gap" filled with void water. Here $\eta(t)$ is the time-dependent well-mixed concentration of the soluble species in the water in the void. To solve for $\eta(t)$, the mass balance in the void is

$$V\frac{d\eta(t)}{dt} = \dot{m}_f(t) - \dot{m}(t) - \lambda V \eta(t), \qquad t > 0 \qquad (5)$$

where $\dot{m}_f(t)$ is the rate of dissolution of the species from the UO_2 grains into the void volume V, and $\dot{m}(t)$ is the rate of species migration into the rock. To solve (5), we use the initial condition

$$\eta(0) = \eta^\circ \qquad \text{as specified} \qquad (6)$$

where η° is the initial concentration of the species in the void water. The mass flux at the interface between the internal void space and the porous rock is

$$\dot{m}(t) = -SD\epsilon \frac{\partial c(a,t)}{\partial x} \qquad (7)$$

To obtain the solution, we made the following additional assumptions,
• The UO_2 matrix can be considered stable;
• In terms of release from the matrix or UO_2 grains, the release of the species is congruent with the release rate of the controller species, such as UO_2 itself.

The solution is

$$\eta(t) = \eta^\circ e^{-\lambda t} F(\beta^2 t) + c_s \frac{M^\circ}{M_c^\circ}\sqrt{\frac{K_c}{K}}\beta\left[1 - F(\beta^2 t)\right]e^{-\lambda t},$$

$$t > 0 \qquad (8)$$

where

$$\beta \equiv \sqrt{\frac{KD\epsilon^2}{a^2}}$$

and

$$F(\beta^2 t) = e^{\beta^2 t}\text{erfc}\{\sqrt{\beta^2 t}\}$$

and M° is the inventory of the species and the subscript c stands for the controller. The solution for the concentration of the species in the field is

$$c(x,t) = \eta^\circ e^{-\lambda t} e^{\beta\sqrt{K/D}(x-a)} e^{\beta^2 \tau}$$

$$\times \text{erfc}\left(\beta\sqrt{t} + \frac{\sqrt{K/D}(x-a)}{2\sqrt{\tau}}\right)$$

$$+ c_s \frac{M^\circ}{M_c^\circ}\sqrt{K_c/K}\beta F(\beta^2 t)e^{-\lambda t}, \qquad t > 0 \qquad (9)$$

The mass transfer rate is

$$\dot{m}(t) = \eta^\circ \beta V e^{-\lambda t}\left\{\frac{1}{\sqrt{\pi t}} - \beta F(\beta^2 t)\right\}$$

$$+ \beta \int_0^t e^{-\lambda \tau}\left\{\frac{1}{\sqrt{\pi \tau}} - \beta F(\beta^2 \tau)\right\}d\tau \qquad (10)$$

from which the fractional release rate can be calculated.

An engineered backfill can be used as part of the waste package. In the case of the vertical waste package emplacement mode at Yucca Mountain, the air gap between the waste package and the emplacement hole wall can become filled with rubble or sediments and we can analyze the fractional release rate as if a backfill exists. In this case the situation is as shown in Figure 1b. The backfill thickness is b. We define the origin at the interface of the two layers.
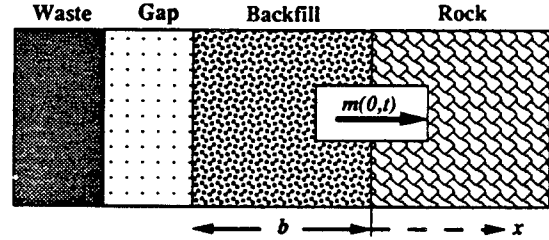

Figure 1b. Release of Soluble Species into Backfill and Rock

The governing equations are[8]

$$\frac{\partial c_1}{\partial t} = D_1 \frac{\partial^2 c_1}{\partial x^2} - \lambda c_1, \quad -b < x < 0, t > 0, D_1 \equiv \frac{D}{K_1} \qquad (11)$$

$$\frac{\partial c_2}{\partial t} = D_2 \frac{\partial^2 c_2}{\partial x^2} - \lambda c_2, \quad x > 0, t > 0, D_2 \equiv \frac{D}{K_2} \qquad (12)$$

where the subscripts 1 and 2 refer to the layer closer to the waste and further away respectively.

The side conditions are

$$c_1(x,0) = 0, \qquad -b < x < 0, \qquad (13)$$

$$c_2(x,0) = 0, \qquad x > 0, \qquad (14)$$

$$c_1(0,t) = c_2(0,t), \qquad t \geq 0 \qquad (15)$$

$$-\epsilon_1 D\frac{\partial c_1}{\partial x} = -\epsilon_2 D\frac{\partial c_2}{\partial x} \qquad at \quad x = 0, t \geq 0 \qquad (16)$$

$$c_2(\infty,t) = 0, \qquad t \geq 0 \qquad (17)$$

2

We assume the water in the void volume V to be well-mixed and thus the species concentration at the inner surface of the backfill is the same as that in the void volume, resulting in the mass balance (with $S = V/a$)

$$-V\frac{\partial c_1(-b,t)}{\partial t} = -D\epsilon_1 S\frac{\partial c_1(-b,t)}{\partial x} + \lambda V c_1(-b,t), t \geq 0$$
(18)

The initial concentration of the readily soluble species in V is taken to be

$$c_1(-b,0) = \eta^\circ \qquad \text{as specified} \qquad (19)$$

The mass transfer rate at the backfill/rock interface is

$$\dot{M}(0,t) =$$

$$2K_1\epsilon_1\eta^\circ S\frac{e^{-\lambda t}}{(\delta+1)}\sum_{n=0}^{\infty}\left[\sqrt{\frac{D_1}{\pi t}}\exp\left\{\frac{(-2n+1)^2 b^2}{4D_1 t}\right\}\right.$$

$$-\gamma D_1 \exp\left\{(2n+1)b\gamma + D_1\gamma^2 t\right\}$$

$$\left.\times \text{erfc}\left\{\frac{(2n+1)b}{2\sqrt{D_1 t}} + \gamma\sqrt{D_1 t}\right\}\left(\frac{\delta-1}{\delta+1}\right)^n\right], t \geq 0 \quad (20)$$

where

$$\delta = \sqrt{\frac{K_1}{K_2}\frac{\epsilon_1}{\epsilon_2}} \qquad \gamma = K_1\epsilon_1 S/V \qquad (21)$$

The fractional release rate is obtained by dividing the mass flux by the 1000-year inventory of the species.

The details of the solutions can be obtained from the authors.

RESULTS

We illustrate the analytic results using conditions typical of a nuclear waste repository at Yucca Mountain. Table I lists dimensions of the waste package.[2,9] Table II lists assumed properties of the tuff and backfill.[2,10] Table III lists characteristics of the nuclides used in the calculations.

Table I. Waste Package Dimensions, Spent Fuel from PWR

Height	(m)	4.76
Radius	(m)	0.33
Thickness of Gap	(cm)	15.0
Volume of Gap	(m³)	1.5

Table II. Tuff Properties

Diffusion Coefficient	cm²/s	10^{-6}
Porosity in Tuff		0.14
Porosity in Backfill		0.3

Table III. Characteristics of the Nuclides Studied

	Cs-135	I-129	Tc-99
R_d (cm³/g)	600	0	0
Decay Constant(a⁻¹)	2.3×10^{-7}	4.1×10^{-8}	3.3×10^{-6}
Calculated USNRC Release Limit (a⁻¹)	5.0×10^{-5}	5.5×10^{-4}	1.0×10^{-5}

The retardation coefficient for cesium is calculated from sorption ratios in column tests.[2] Different retardation coefficients have been calculated for backfill and tuff using the relationship.

$$K = 1 + R_d\rho\frac{1-\epsilon}{\epsilon} \qquad (22)$$

where the bulk density ρ has been taken to be 2.5 g/cm³. The porosity value for tuff is taken from *Reference Waste Package Environment*.[10]

In Figures 2, 3, 4 & 5 we show the calculated fractional release rates of ^{135}Cs, ^{129}I and ^{99}Tc to the surrounding tuff as a function of time for no backfill and 10-cm and 30-cm of backfill. These results apply for failure and the beginning of release from emplacement to 5,000 years. These results have been calculated using (20) and the releases are due to the instant release fractions only. Here the fractional release rate of a species is obtained by calculating the mass release rate and dividing by the 1000-year inventory of that species. Also shown in the figures is the USNRC release rate limit for ^{99}Tc,[1] and the calculated release rate limits for ^{135}Cs and ^{129}I.

The fractional release rate curves for ^{135}Cs, in Figure 2, begin at a higher fractional release and greater negative slope than those for ^{99}Tc and ^{129}I, because of the greater sorption of cesium in the surrounding tuff. The higher early release rate of cesium depletes the inventory of soluble cesium in the void water and soon results, after a few years, in a cesium fractional release rate lower than that of technetium and iodine. If the readily soluble fraction of cesium is only a few percent, the calculated release limit for ^{135}Cs is exceeded only for a few years, assuming that all waste packages fail at the same time. A distribution of container failures over several decades can result in a repository-average fractional release rate of cesium below the calculated limit, for soluble fractions of a few percent. A 10-cm thick layer of backfill delays the arrival of the ^{135}Cs peak by several decades and for bare waste, the calculated limit is exceeded for only a brief time. A 30-cm thick backfill reduces the peak fractional release rate to below the calculated limit.

For the same readily soluble fractional inventory, the fractional release rate curves for ^{99}Tc and ^{129}I, Figures 3 and

4, are identical for times up to about 100,000 years, because both species are assumed to be non-sorbing. At later times, the fractional release rates for ^{99}Tc become smaller because of its shorter half life.

For soluble fractions of a few percent, the release-rate limit for ^{99}Tc is exceeded for several hundred years, if all containers fail simultanously. Here the backfill is of little help in meeting the release rate limit because ^{99}Tc and ^{129}I are non-sorbing. Container failures distributed over about a thousand years could result in a repository-average fractional release rate below the regulatory limit.

Figure 5 shows the fractional release rates of all three soluble species for the case of no backfill, if ten percent of their respective inventories are released at failure time. This initial amount of the species in the gap is consistent with the estimates of Garisto et al.[7] For ^{135}Cs and ^{129}I, the USNRC release rate limit is exceeded for only a couple of decades, even with these conservative assumptions of bare waste and water-saturated repository. For ^{99}Tc, the USNRC limit is exceeded for up to thousands of years. However, for the more realistic cases of a container or if the container failures were distributed over time, the calculated fractional release rates would probably fall below the USNRC limit.

Figure 6 shows the composition of the fractional release rate of ^{135}Cs, from the instant release fraction, from the waste matrix and the total release, calculated using (10). Release congruent with the dissolving uranium matrix is assumed, with a uranium-matrix solubility of 4×10^{-3} moles/L.[2] The oxidizing condition at Yucca Mountain causes a high matrix solubility, so that matrix dissolution dominates the fractional release rate. Figure 6 shows that for bare waste in contact with water, and using an oxidizing uranium solubility, the fractional release rate of ^{135}Cs falls below the calculated limit within tens of years of water penetration.

CONCLUSIONS

These calculations are from a bounding analysis that conservatively assumes bare spent fuel, with water in waste-package voids and in contact with saturated tuff. Because the container, fuel cladding, and corrosion products can still present diffusion barriers after the containers and cladding fail, the more realistic release rates are expected to be less than those calculated here. Calculations of the effects of these additional barriers are in progress.

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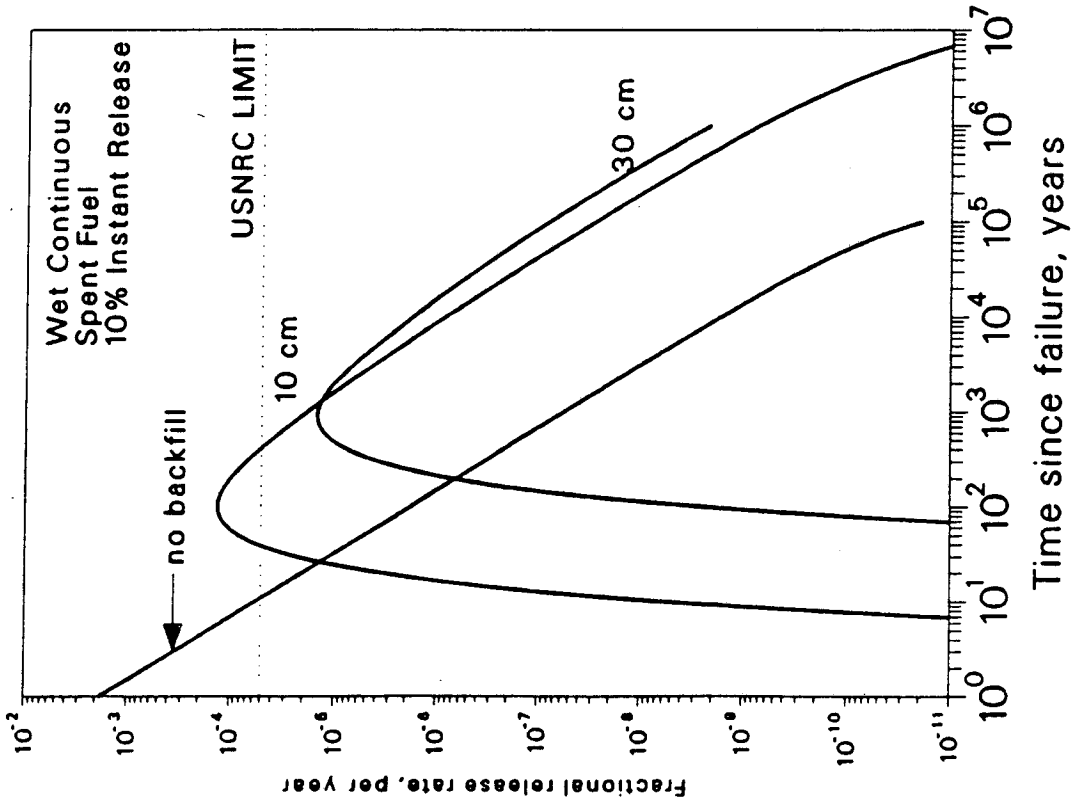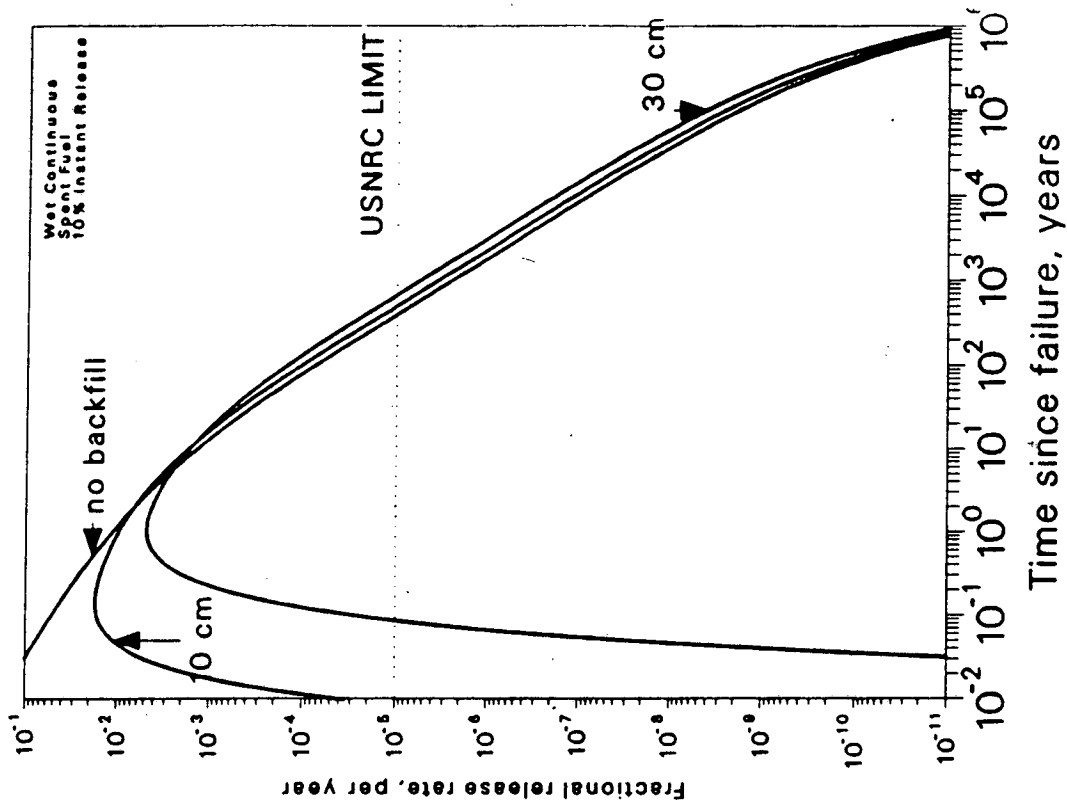
Figure 3. Fractional Release Rate of Tc-99

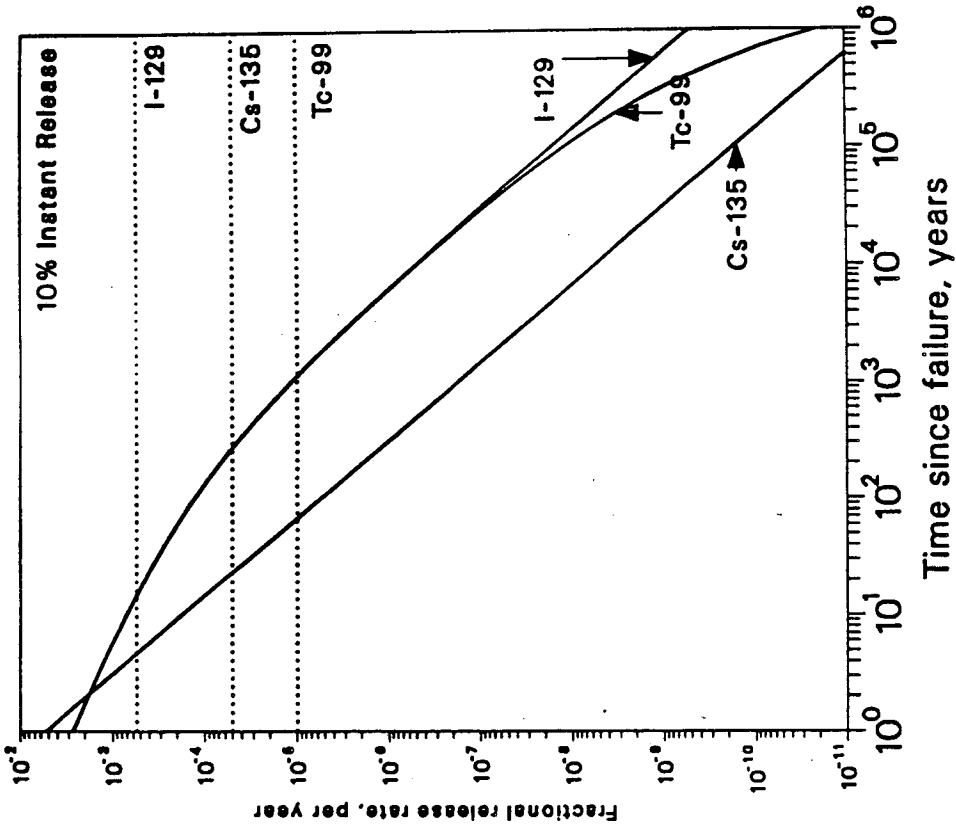Figure 2. Fractional Release Rate of Cs-135

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Figure 5. Fractional Release Rates of Soluble Species
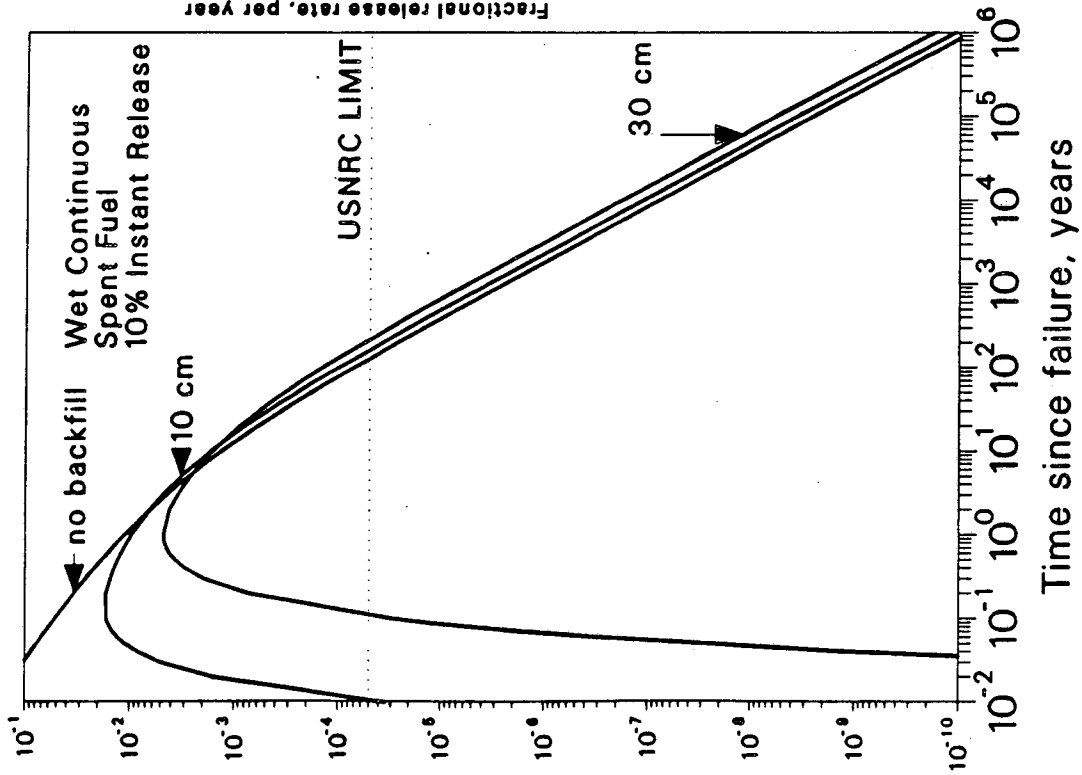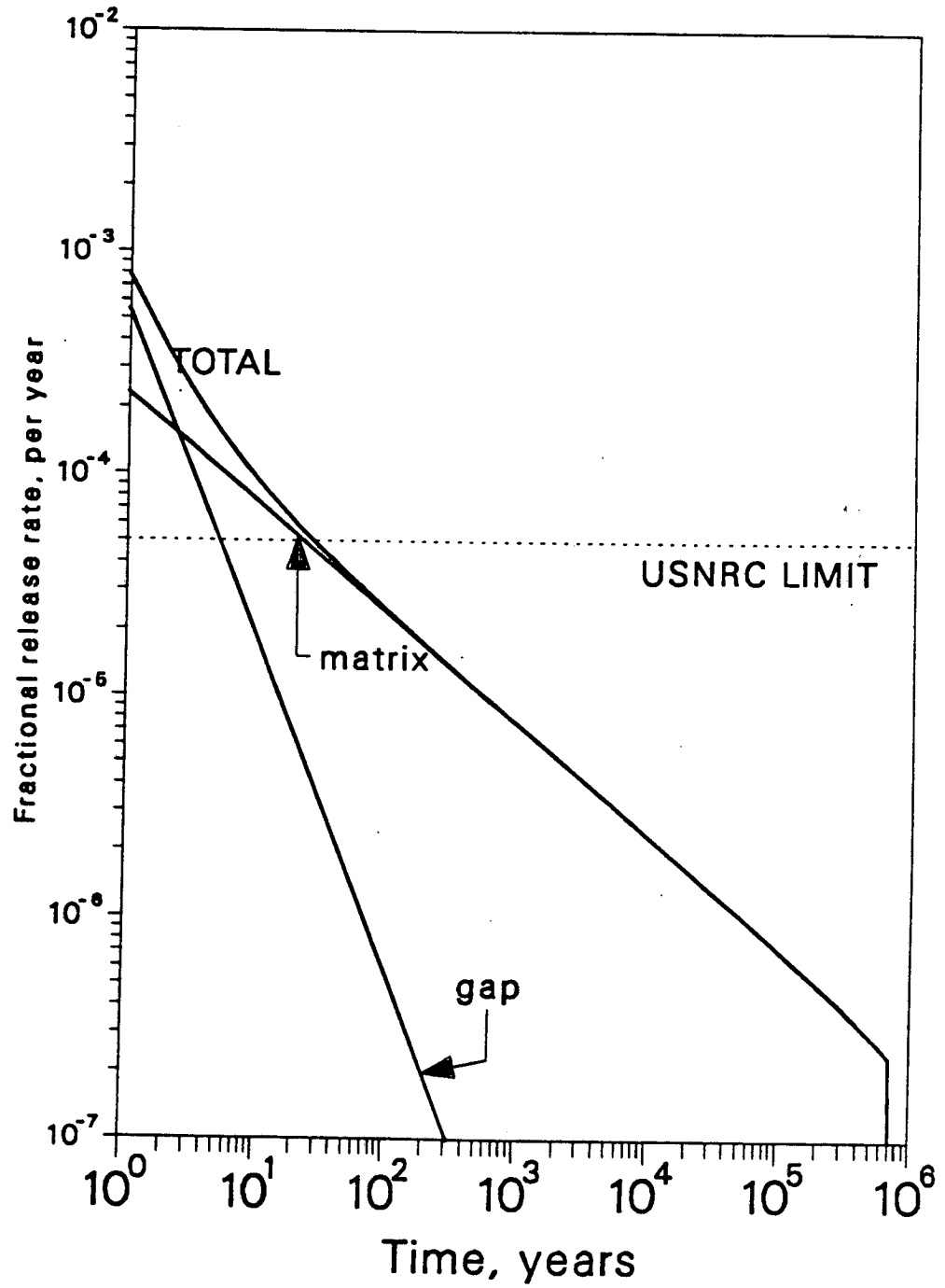

Figure 4. Fractional Release Rate of I-129

6

Figure 6. Composition of the Fractional Release Rate of Cs-135