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^{14}C Release From Failed Spent Fuel Containers

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ABSTRACT

Partially failed containers may provide a meaningful barrier to the release of gaseous $^{14}\text{CO}_2$. A modeling approach is outlined and sample calculations are provided that show the effect on release due to a limited perforation area, to decreasing temperature, and to partial occlusion of the perforated area by corrosion products.

TABLE OF CONTENTS

	page
1. INTRODUCTION	1
2. MODELING FORMALISM	2
2.1 Isothermal, diffusive releases	5
2.1.1 Prompt oxidation, no tail	5
2.1.2 Prompt oxidation followed by a decaying tail	6
3. NUMERICAL RESULTS	6
4. CONCLUSIONS	10
5. REFERENCES	11

1. INTRODUCTION

For licensing of spent fuel waste packages the fate of volatile species containing ^{14}C must be considered [Van Konynenburg, 1987]. The ^{14}C inventory at discharge in a 17x17 PWR spent fuel assembly with 33,000 MWd/MTHM burnup is 1.548 curies/MTHM. Roughly 38% of the ^{14}C will reside in the UO_2 pellets; 62% is associated with the rest of the assembly materials (*cladding waste*). Because of its long half-life (5730 years), the ^{14}C inventory is only slightly reduced over the first few thousands years in the repository.

Because of its presence in the cladding waste, ^{14}C can be released from the spent fuel as soon as a container is breached. The most important mechanism for ^{14}C detachment from cladding waste surfaces is its oxidation, in air, into $^{14}\text{CO}_2$. From the latest version of the Site Characterization Plan (SCP) of the Yucca Mountain site, Nevada, [DOE, 1988] the following prompt oxidation fractions, f , of the total ^{14}C inventory within the spent fuel can be deduced:

$$\begin{aligned} f &= 1\% \text{ for } T > 215^\circ\text{C} \\ f &= 0.2\% \text{ for } 170 < T < 215^\circ\text{C} \\ f &\leq 0.1\% \text{ for } T < 170^\circ\text{C} \end{aligned}$$

These prompt oxidation fractions, however, may have to be augmented further, by adding 2%, at least, to reflect recent experimental data under both oxidizing and "inert" conditions.

The SCP suggests that the $^{14}\text{CO}_2$ is released *instantly* from the breached container. Under this assumption, exceedingly few containers can fail per year if the applicable performance criteria are to be met. A sample calculation to address the Nuclear Regulatory Commission (NRC) substantially complete containment (SCC) standard of 10 CFR 60 is given below. To that effect, since 100% absence of container failures cannot be demonstrated, we assume that a certain number of containers can fail provided the ^{14}C annual release from the ensemble of waste containers is confined to 10^{-6} of the total ^{14}C inventory in any given year.

Sample calculation

Assume that 70,000 MTHM of spent fuel have to be disposed of, all in the form of PWR 17x17 assemblies with a burnup of 33,000 MWd/MTHM. Assuming also that there are six spent fuel assemblies per container, one obtains a ^{14}C inventory of 4.285 curies per container and a total number of 25,285 containers.

There will be then $1.084 \cdot 10^5$ curies of ^{14}C in the repository of which, in the SCC period, only one millionth are allowed to escape per year. Therefore the total allowable release of ^{14}C from the repository during the SCC period is 0.108 curies/year.

0.108 curies correspond to 2.5% of the total ^{14}C inventory of a **single** container. That means that **not even one** container/year can be allowed to fail or, **at most**, one, considering a prompt oxidation fraction of roughly 2.5%.

It can be argued, however, that prompt oxidation of ^{14}C into $^{14}\text{CO}_2$ should not necessarily result in prompt release of all the oxidized fraction out of the spent fuel containers unless the perforated area in the container surface is large enough. In other words, a small average perforation area with respect to the total surface area of the container could still guarantee that the release is slow enough to allow many more than one container to fail per year. This aspect of ^{14}C release is examined in the present progress report.

2. MODELING FORMALISM

Upon performing a $^{14}\text{CO}_2$ mass balance within a single container, the following equation can be written in terms of $N(t)$, the number of $^{14}\text{CO}_2$ molecules in the empty volume within the container:

$$dN/dt = - [J_D(t) + J_C(t)] \cdot A(t) - \lambda \cdot N(t) + S(t) \quad (1)$$

where $J_D(t)$ represents the diffusive mass flux (per unit area) away from the container, $J_C(t)$ is the convective mass flux, $A(t)$ is the area of the penetration as it evolves with time, $\lambda \cdot N(t)$ is the removal rate due to decay, and $S(t)$ is the production rate of $^{14}\text{CO}_2$ due to oxidation of the ^{14}C .

Ideally, the rate of ^{14}C oxidation into $^{14}\text{CO}_2$ is dependent on the rate of supply of O_2 . We assume, *conservatively*, that as soon as the perforation penetrates the container all the oxygen needed to oxidize the ^{14}C is instantly available and instantly replenished. One can assume several $^{14}\text{CO}_2$ production rate functions. From the SCP, the following one can be deduced:

$$S(t) = G(T) \cdot \delta(t-t_0) \quad (2)$$

where the function $\delta(t)$ represents Dirac's delta and T the temperature, itself a function of time. Alternatively, if one wants to model a prompt oxidation step followed by a decaying exponential tail, one may assume that:

$$S(t) = S_o \exp[-\alpha(T) \cdot (t-t_o)] U(t-t_o) \quad (3)$$

with $U(t)$ the Heavyside step function and α an experimental parameter.

The diffusive term, $J_D(t)$, can be obtained from the literature [Aidun, 1987]. The steady-state, diffusive release of a solute per unit area from a cylindrical hole into an infinite medium can be represented as follows:

$$J_D(t) = \frac{D(T) N(t)}{V \cdot \{ \ell \epsilon^{-1} + 0.25 \cdot [\pi A(t)]^{\frac{1}{2}} \}} \quad (4a)$$

where:

- $D(T)$ - temperature-dependent diffusion coefficient
- V - gas volume within the container
- ϵ - open porosity of the hole
- ℓ - container wall thickness (penetration length)
- $A(t)$ - hole perforation area as function of time

Usage of the above expression for the diffusive flux assumes that the concentration profile within the cylindrical penetration adjusts itself instantly to a steady-state type profile. This assumption is justified *a posteriori* noting that the diffusion coefficient is large enough to assure rapid establishment of a steady-state profile.

Since $\ell \approx 1$ cm in Eq.(4a), the dependence of J_D on A , the hole perforation area, is negligible as long as the following inequality is satisfied:

$$A \ll 5.1 \epsilon^{-2}, [A] \text{ in } [\text{cm}^2], \quad (4b)$$

or, alternatively, in terms of the diameter, d , of the perforation area of the hole:

$$d \ll 2.5 \text{ } \epsilon^{-1}, [d]=[\text{cm}]. \quad (4c)$$

This is likely the case in our applications. Combining the latter observation with the fact that, for non-solubility-limited release, holes next to each other on a container surface do not interact significantly with each other (see also [Pescatore, 1987]), one can model the release from multiple holes as if it occurred from a single, equivalent hole with the same combined surface area or the equivalent diameter.

Equation (4a) can be written alternatively as:

$$J_D(t) = F_D(T,t) N(t) \quad (5a)$$

with

$$F_D(T,t) = \frac{D(T)}{V \cdot \{ \ell \text{ } \epsilon^{-1} + 0.25 \cdot [\pi A(t)]^{\frac{1}{2}} \}} \quad (5b)$$

At the present stage of our study we have yet to model the convective flux contribution. Under normal conditions the ΔP of $^{14}\text{CO}_2$ across the waste container is negligible as it is confined to values within $5 \cdot 10^{-3}$ atm. A proper expression for $J_C(t)$ will be necessary, however, in order to establish the importance of container "breathing" due to (a) pressure variations in the outside environment and (b) occasional pressure surges due to failing fuel rod cladding. Since in both cases the potential release should be proportional to the amount of $^{14}\text{CO}_2$ present in the container, it can be argued that a general expression for $J_C(t)$ is of the form:

$$J_C(t) = F_C(T) N(t), \quad (6)$$

with $F_C(T)$ a function yet to be defined. Therefore the $^{14}\text{CO}_2$ mass balance equation can be recast as follows:

$$dN/dt = - H(T,t) N(t) + S(t) \quad (*7a)$$

where

$$H(T,t) = \lambda + (F_D + F_C) A(t) . \quad (7b)$$

The general solution to Equation (7a) is:

$$N(t) = e^{-\int H dt} \cdot \{ \int [S e^{+\int H dt}] dt + \text{constant} \} \quad (8)$$

in which the value of the arbitrary constant is determined by the initial conditions to the problem.

Equation (8) can be substituted into Equations (4a) and (6) to obtain the rate of release per unit area of the penetration. The latter expressions can then be integrated to obtain cumulative releases.

2.1 Isothermal, diffusive releases

At this time, we have produced two solutions to Equation (7.a). In both cases we do not model convection ($F_C=0$) and we assume (a) isothermal conditions and (b) a fixed size perforated area forming at time $t=0$. In one case we investigate prompt oxidation of the ^{14}C into $^{14}\text{CO}_2$; in the other case we investigate prompt oxidation followed by an additional, exponentially decaying tail according to Equations (2) and (3), respectively.

2.1.1 Prompt oxidation, no tail

Combining Equation (2) with Equation (8) and imposing the initial condition $N(0)=0$, and letting $t_0 \rightarrow 0$, the solution to Equation (8) is very simply an exponential function. Namely:

$$N(t) = G(T) \cdot \exp[-(\lambda + F_D(T)A) \cdot t], \quad t > 0. \quad (9)$$

An interesting aspect of the latter expression is that the amount of $^{14}\text{CO}_2$ species left in the container at time t , as well as its rate of change with time, vary exponentially with the total perforated area of the container.

2.1.2 Prompt oxidation followed by a decaying tail

Combining Equation (3) with Equation (8) and imposing the initial condition $N(0)=0$, and letting $t_0 \rightarrow 0$, the function $N(t)$ assumes the following form:

$$N(t) = [S_o/(\lambda + F_D A - \alpha)] \cdot \{\exp[-\alpha \cdot t] - \exp[-(\lambda + F_D A) \cdot t]\}, \quad t \geq 0. \quad (10)$$

Defining

$$\beta = \lambda + F_D A \quad (11a)$$

it can be shown that $N(t)$ and, consequently, $J_D(t)$, attain their maximum values at the time:

$$t_{\max} = \frac{\ln(\beta/\alpha)}{\beta - \alpha} \quad (11b)$$

At that time:

$$N_{\max} = \frac{S_o}{\beta - \alpha} \cdot [(\alpha/\beta)^{\alpha/(\beta-\alpha)} - (\alpha/\beta)^{\beta/(\beta-\alpha)}] \quad (12)$$

from which $J_{D,\max}$ can be inferred.

3. NUMERICAL RESULTS

With reference to the release problem identified in Section 1, we now address the question: what the average perforation area (or its *equivalent* diameter) should be in spent fuel containers so that $0 \pm \%$ (i.e., 25 containers) can fail simultaneously in a year and still meet a 10^{-6} release limit per year from the repository during the substantially complete containment period. *Similar calculations can be performed for the controlled release period.*

In order to address that problem we have subdivided the repository into different temperature zones where we hold the temperature constant with time. We did not take one conservative temperature for the whole repository as the consequence for this case can also be inferred from the numerical results reported hereafter.

We have taken four temperature zones with $T_{av} = 250$, $T_{av} = 190$, $T_{av} = 150$, and $T_{av} = 80$ °C, respectively, and for each temperature regime we have assessed the influence on release due to crud potentially occluding part of the perforation area (the higher the degree of occlusion, the smaller the value of the open porosity parameter). We have assumed also a prompt oxidation fraction of 2% plus the SCP suggested fraction. Then we have allowed a slow oxidation fraction of up to 1% during the first 15 days after breach. Our results are reported in Tables 1 through 4.

Taking Table 1 as the reference, these tables are interpreted as follows: if the average perforated area per container is such that its equivalent diameter is below 0.48 mm, the 10^{-6} criterion is met even if (a) up to 0.1% of the containers fail simultaneously, (b) there is no crud in the hole ($\epsilon = 1$), and (c) up to 4% of the total, original ^{14}C inventory oxidizes (3% promptly + 1% in the tail) within two weeks. Lower temperatures or higher degrees of hole occlusion ($\epsilon < 1$) would allow larger penetration diameters (areas), as can be inferred from the calculated data.

In these calculations the diffusion coefficient of $^{14}\text{CO}_2$ in air was taken as the same as that of CO_2 in nitrogen [Perry, 1984], namely:

$$D(T) = 0.0245 \cdot T^{1.75}, \quad [D] = [\text{m}^2/\text{yr}], \quad [T] = [\text{°K}].$$

The gas volume within the container was taken to be 1 m^3 . Tortuosity, τ , was taken into account as function of open porosity, ϵ , as follows:

$$\tau = 1 - 4 \cdot \log_{10}(\epsilon).$$

Tables 1 to 4 suggest that, if no earlier penetrations have occurred, one could still tolerate a **0.1%** failure of all containers (i.e., **25** containers in the hypotheses of the problem indicated in Section 1) in a given year provided the equivalent diameter of the average perforated area per container is within the calculated limits. These limits vary from half a millimeter to about 28 millimeters depending on

Table 1. Perforated area equivalent diameter in millimeters in order to meet a 10^{-6} release/year criterion assuming 0.1% of the containers fail simultaneously.

$T_{av} = 250\text{ }^{\circ}\text{C}$
prompt oxidation fraction = 3%
 Δf - further oxidation fraction over 15 days
 ϵ - open porosity of the hole

Δf	0.05%	0.1%	1%
ϵ			
1	0.55	0.55	0.48
0.1	3.87	3.86	3.39
0.01	16.43	16.30	14.34

Table 2. Perforated area equivalent diameter in millimeters in order to meet a 10^{-6} release/year criterion assuming 0.1% of the containers fail simultaneously.

$T_{av} = 190\text{ }^{\circ}\text{C}$
prompt oxidation fraction = 2.2%
 Δf - slow oxidation fraction over 15 days
 ϵ - open porosity of the hole

Δf	0.05%	0.1%	0.2%
ϵ			
1	0.72	0.71	0.69
0.1	5.05	4.99	4.89
0.01	21.30	21.07	20.62

Table 3. Perforated area equivalent diameter in millimeters in order to meet a 10^{-6} release/year criterion assuming 0.1% of the containers fail simultaneously.

$T_{av} = 150\text{ }^{\circ}\text{C}$
prompt oxidation fraction = 2.1%
 Δf - further oxidation fraction over 15 days
 ϵ - open porosity of the hole

Δf	0.01%	0.05%	0.1%
ϵ			
1	0.80	0.80	0.79
0.1	5.65	5.60	5.53
0.01	23.82	23.60	23.33

Table 4. Perforated area equivalent diameter in millimeters in order to meet a 10^{-6} release/year criterion assuming 0.1% of the containers fail simultaneously.

$T_{av} = 80\text{ }^{\circ}\text{C}$
prompt oxidation fraction = 2.1%
 Δf - further oxidation fraction over 15 days
 ϵ - open porosity of the hole

Δf	0.01%	0.05%	0.1%
ϵ			
1	0.94	0.93	0.92
0.1	6.63	6.57	6.49
0.01	27.93	27.66	27.35

temperature, the amount of crud present in the perforation, and the ^{14}C oxidized fraction. The presence of crud partly occluding the perforation is an important component of our models.

4. CONCLUSIONS

Our preliminary analysis supports the assumption that partly failed containers may offer a significant delay to gaseous ^{14}C release both during the substantially complete containment and the controlled release periods.

So far, our analysis can model (a) the finite amount of ^{14}C present in the spent fuel container, (b) container wall thickness (c) perforated area equivalent diameter and growth rate, (d) degree of occlusion of the perforation due to corrosion products, (e) thermal oxidation rate of the ^{14}C into $^{14}\text{CO}_2$, (f) gaseous diffusion of the $^{14}\text{CO}_2$ in the (partly occluded) hole(s), and (g) radioactive decay. All rate processes can be implemented with their temperature dependence. Further work is needed to incorporate "breathing" of the container caused by barometric pressure variations in the outside environment and the effect of occasional pressure surges due to failing fuel rods. Once these analyses are completed, the relevant expressions for ^{14}C release should be convoluted with the container breach rate distribution functions that are being developed within the waste management community. One such analysis will identify the allowable container perforation area in order to meet the applicable performance criteria.

The results of the ^{14}C release analyses from failed containers could be also verified via gas diffusion experiments, which are amply within reach of available technology.

The approach proposed here for gaseous radionuclide release can also be proposed for the release of radionuclides potentially leached by groundwater infiltrating a breached container. The likely presence of crud in container penetrations may allow only very small releases *regardless* of radionuclide solubilities. This would be an important effect during the NRC-regulated (10 CFR 60) controlled release period.

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