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Dr. Ramesh Dayal, Guest Editor  
Ontario Hydro Technologies  
800 Kipling Avenue  
Toronto, Ontario, Canada M8Z 5S4

Dear Dr. Dayal:

I have revised my manuscript, "Long-Term C-14 Source Term for a High-Level Waste Repository" (#40208-096) according to the reviewers' comments. Before the revision, I had a discussion with one of the reviewers, S. Stroes-Gascoyne, about the comments. During this discussion, we did not find any technical conflicts. The results of this discussion have been addressed adequately in the revision. Regarding editing, I have revised all marked-up words and sentences. Also, I have revised many other sentences and paragraphs carefully, to write a more smoothly flowing paper and to convey the message clearly and succinctly. One of the NRC editors has reviewed the revised manuscript.

Detailed technical revisions follow, along with a marked-up copy of the manuscript.

1. For readers from outside the United States, more explanations have been provided about the disposal concept of high-level waste in the proposed Yucca Mountain site. The engineered barrier system (EBS) (pages 2 and 3), repository temperatures (page 3), oxidizing (page 4) and near-static environments (pages 12 and 14), and backfill (page 3) have been addressed.
2. I have justified the use of data, at various temperatures (page 4). Also, I have included appropriate discussions on the effects of temperature throughout the paper (see example on page 6).
3. I have included detailed explanations regarding: (a) fission product releases (page 13); and (b) uncertainties with the analysis of the altered layer of the spent fuel (SF) matrix (page 13).
4. I have also presented detailed procedures regarding quantitative assessments vis-à-vis the SF matrix for: (a) solubility-controlled dissolution and (b) diffusion-limited dissolution (pages 15 and 16).
5. The tenuous conclusions have been revised, according to the accepted content of the abstract.
6. Literature citations have been confirmed; mistyped Tables 3 and 4 have been corrected.
7. All redundant contents have been deleted; a few numerical values have been updated, including oxidation rates of Zircaloy and dissolution rates of SF matrices.

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8. Other points incorporated include:
- Infrequent abbreviations have been deleted;
  - The authors of the original articles have been cited for the grain boundary inventory of C-14. I have deleted Stroes-Gascoyne, et al., who had presumably cited the numerical values from the original articles in their paper (page 5). I have also deleted the redundant C-14 inventory on the SF surface.
  - Appropriate articles have been cited, with a short discussion about radiation effects in precipitated materials. The reviewer's comments were about the radiolysis effects on the dissolution of the SF matrix. On the other hand, this paper addresses the radiolysis effects on the integrity of the altered layer (page 13).
  - The quotation of  $U_3O_8$  in the discussion of metals has been deleted, to avoid confusion. Also, discussions on research activities about  $U_3O_8$  formation have been deferred until published documents are available.
  - Following the NRC staff's recommendation, discussion on analogue studies has been deferred until we understand the subject matter more clearly.
  - The dissolution of carbides (or oxycarbides) has been explained (page 13).
  - The controlled C-14 release by through-wall pits has been addressed to introduce the pitting corrosion of the inner layer of the container (page 18).
  - Some terminologies have been explained, such as rim effects (page 5), dissolving phase and altered phase (page 13), light elements (page 6), diffusion (pages 5 and 14), and types of Zircaloy (page 10). "Reprecipitates" have been replaced by either "precipitated materials" or "altered layer" (page 13).

I appreciate my opportunity to participate in this special issue of C-14 management.

Sincerely,

Tae M. Ahn  
 Engineering and Material Section  
 Engineering and Geosciences Branch  
 Division of Waste Management  
 Office of Nuclear Material Safety  
 and Safeguards

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**LONG-TERM C-14 SOURCE TERM FOR A HIGH-LEVEL WASTE REPOSITORY**

**Tae M. Ahn  
U.S. Nuclear Regulatory Commission  
Washington, DC 20555-0001, USA**

## ABSTRACT

This paper evaluates the possibility of long-term C-14 releases from spent fuels and containers in the anticipated environments of the proposed Yucca Mountain high-level waste repository. Long-term degradation mechanisms of spent fuel matrices, cladding, and containers are evaluated. Under dry conditions, formation of higher oxides, such as  $U_3O_8$ , may lead to significant C-14 releases from the spent fuel matrix. It is unclear whether there will be significant C-14 releases from lower oxidation to  $UO_{2.4}$  or from the unoxidized matrix. Under aqueous dissolution conditions, C-14 releases from the spent fuel matrix can be significant. Under aqueous dissolution or dry conditions, it is unlikely that there will be significant C-14 releases from cladding, unless severe localized corrosion takes place. In considering containers and cladding as metallic barriers, we discuss qualitatively various factors governing total C-14 containment inside metallic barriers. C-14 releases can be delayed, even by the formation of small through-wall pits in metallic barriers. Although we do not have completely definitive information yet, it is clear that the spent fuel matrix, cladding, and containers can serve as important barriers to C-14 releases from waste packages in a repository environment.

### 1. INTRODUCTION

Currently, the United States has one proposed repository site for high-level nuclear waste (HLW). The proposed site is Yucca Mountain, in the southwestern corner of the Nevada Test site (1): characteristics of the site include (a) the static water level at Yucca Mountain is approximately 530 m below the surface; (b) the host rock is a densely welded, devitrified tuff, with some lithophysal cavities; (c) the rock is estimated to contain approximately 5 % water, by volume, with a porosity of approximately 12 %; and (d) the repository horizon is fractured with an average fracture density, 0.8 to 3.9 fractures per meter. Currently, it is planned that the repository be located in a horizon above the water table. Among the advantages of locating a repository in this so-called unsaturated zone is less severe corrosion of waste packages, because of the small amount of water. The current planning is that only two forms of U.S. HLW may go into a tuff repository: (a) spent fuel (SF), from commercial light-water nuclear reactors (LWRs); and (b) HLW glass. The HLW glass is a borosilicate glass containing high levels of fission products from reprocessing commercial SF and from liquid HLW accumulated from three defense installations.

The U.S. Department of Energy (DOE) is responsible for the safe disposal of HLW in Yucca Mountain. DOE's disposal implementation is under the licensing authority of the U.S. Nuclear Regulatory Commission and the applicable environmental standards of the U.S. Environmental Protection Agency (EPA). Current rules mandate that:

(a) Substantially complete containment of radionuclides within the waste packages be ensured for the first 300 to 1000 years after the emplacement of waste packages. The release of any radionuclide from the engineered barrier system (EBS) be controlled so as not to exceed 1 part per 100,000 per year of the inventory of that radionuclide calculated to be present at 1000 years after permanent closure (i.e., 10 CFR 60.113, Nuclear Regulatory Commission (NRC) (2)). The EBS is composed of: (i) waste packages (the waste form and

any containers, shielding, packing, and absorbent materials immediately surrounding an individual container); and (ii) an underground structure, including openings and backfill materials, but excluding shaft, boreholes, and their seals; and

(b) Cumulative release of each radionuclide to the accessible environment, for 10,000 years, be limited to a specific maximum, with a likelihood of less than 1 chance in 10 of exceeding this maximum -- and to 10 times the specified maximum, with a likelihood of less than 1 chance in 1000 (i.e., 10 CFR 60.112 (NRC) (2) and 40 CFR Part 191 (EPA) (3) <sup>1</sup>).

In 1988, DOE published the first version of a site characterization plan (SCP) (4). The SCP describes the detailed geology, hydrology, engineering, and other activities that will be conducted to decide the suitability of the proposed Yucca Mountain site for a repository. In the SCP design of waste packages, thin-walled highly corrosion-resistant containers were proposed as a conceptual design. Anticipated container temperatures of SCP waste packages are approximately 250 to 120° C for 1000 years (250 to 150° C for 300 years). Beyond 1000 years, the temperature falls below approximately 120° C (150° C beyond 300 years). Very recently, DOE has proposed alternate design options for waste packages. Current options for the Advanced Conceptual Design (ACD) include either a lower or a higher thermal load than that for the SCP design (5). For the higher thermal load, it is anticipated that surface temperatures of waste packages will be approximately 190 to 90° C, for 300 to 1000 years, and approximately 140 to 75° C, beyond 1000 years (160 to 75° C beyond 300 years); for the lower thermal load, it is anticipated that surface temperatures of waste packages will be approximately 155 to 60° C for 1000 years (155 to 70° C for 300 years), and approximately 60 to 40° C, beyond 1000 years (70 to 40° C beyond 300 years). Temperatures within waste packages will increase by approximately 20° C after 300 years. Beyond that, this difference between the surface temperature and the inner temperature will decrease. (The calculation of these temperatures is still preliminary (5)). The higher thermal load is expected to minimize water around the waste packages. In options for the ACD, DOE proposes that thick-walled corrosion-allowance overpacks be added to the thin-walled corrosion-resistant SCP containers. The ACD also allows the emplacement of backfill surrounding overpacks.

The environment around waste packages has been described as follows (1,6,7). Immediately after waste package emplacement, the host rock and its associated pore water will undergo a temperature increase. As the temperature rises, water will be driven away from waste packages; when the temperature of porous host rocks rises above approximately 120° C (an estimated maximum value), all the liquid water in the rock will vaporize. The atmosphere in pore spaces and around waste packages will then consist of a mixture of air and steam. As the temperature in the host rock cools below approximately 120° C, water will slowly migrate back into the rock pores. Fractures in the host rock above the

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<sup>1</sup> 40 CFR Part 191 was remanded by the Courts. The technical bases for high-level waste standards are being reviewed by the National Academy of Sciences.

repository could admit episodic surges of water to the hot surfaces of waste packages.

The severity of this episodic wetting is considered to depend primarily on: (a) average repository temperature; (b) temperature distributions among waste packages; and (c) characteristics of backfill. Under these circumstances, C-14 will be released from waste forms: (a) under oxidizing dry conditions ("dry conditions") and (b) under oxidizing aqueous dissolution conditions ("aqueous dissolution conditions"). These two types of conditions may be encountered separately or simultaneously, under repository conditions.

Currently, it is estimated that for spent fuels (SF) of pressurized water reactors, C-14 releases from the SF matrices, SF cladding, and SF assemblies, could be approximately 10 times<sup>2</sup> the regulatory 10,000-year limit for C-14<sup>3</sup>, as imposed by 10 CFR 60.112 and 40 CFR Part 191. This estimate assumes that all C-14 is released from SF to the accessible environment. HLW glass does not contain C-14.

Van Konynenburg and his coworkers provided the original technical basis for C-14 releases, from SF assemblies, under the anticipated conditions of Yucca Mountain (10,11). Their work also includes the dose-based health risks associated with these releases (8). They made the assessments based on total C-14 inventory, with experimental measurements and related theoretical analyses.

In this paper, we focus on long-term C-14 releases, based on SF degradation mechanisms that have not been considered previously. More specifically, we describe potential sources of C-14 releases, upon long-term oxidation and dissolution of SF assemblies in the repository. We also summarize the long-term performance of containers for C-14 containment. The only work on containers, up to now, has been modeling of small perforations in container walls, which have been shown to significantly delay C-14 releases (12-14). This paper summarizes the role of containers (a) under environmental conditions leading to total C-14 containment, and (b) for container (or cladding) failure and subsequent perforation.

If the total C-14 inventory of a repository is released to the accessible environment within 10,000 years, there is a potential that the C-14 release rate itself can exceed the overall regulatory limit of 1 part per 100,000 per year. While the total performance assessment involves compliance with rules for the behavior of all radionuclides and it involves both the EBS and natural barriers, in this paper we will discuss potential sources of only C-14 releases from the SF matrix, the SF cladding, and the container, separately. Throughout this paper, we will discuss some data at temperatures other than anticipated repository temperatures. This is done when: (a) we can extrapolate the data to the anticipated repository conditions; (b) we can

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<sup>2</sup> UO<sub>2</sub> matrices: 0.53 Ci/MTHM; Zircaloy: 0.16 Ci/MTHM; and Fuel Assembly: 0.19 Ci/MTHM (We converted the inventory per MTHM of pressurized water reactor SF in references 8-11 to the inventory per MTHM.).

<sup>3</sup> 0.1 Ci/MTHM (3).

discuss C-14 release mechanisms under the anticipated repository conditions based on such data; (c) such data are potentially useful under unanticipated repository conditions; and (d) the data are potentially useful to optimize waste package design. We will similarly discuss effects of other environmental variables such as oxygen partial pressure.

## 2. RELEASE FROM SPENT FUEL MATRICES AND CLADDING

We will treat C-14 releases under dry conditions and under aqueous dissolution conditions separately, primarily because they have different modes of C-14 releases. Instantaneous releases are better understood than long-term releases (11,15-17). Significant rim effects in high-burnup SF may increase instantaneous releases. Rim effects are primarily characterized by a loss of optically definable grain structure and a high volume of small intragranular porosity (18). The inventory from gaps and grain boundaries (excluding the cladding exterior) has been reported to be from 0.05 to 7.3 % of the total inventory in bare and hole-defected moderate-burnup SF of pressurized water reactors (15,16,19). However, virtually no data are available regarding the inventory of grain boundaries in cladding alone. This paper will focus on long-term releases from matrices and cladding of moderate-burnup SF of pressurized water reactors, rather than on instantaneous releases from surfaces, gaps, or grain boundaries.

### 2.1. Release from Spent Fuel Matrices and Cladding under Dry Conditions

Under dry conditions, we believe that C-14 is released either from C-14 (solid-state) diffusion in unoxidized phases or from oxidation processes. A third cause may be the disintegration of SF matrices or cladding through other, less well known, processes such as helium buildup (20). We will only consider diffusion and oxidation, in this paper, because helium buildup is only beginning to be understood. Also, we will discuss SF matrices and cladding separately, because the degradation mechanisms for these two materials differ.

#### 2.1.1 Spent Fuel Matrices

SF matrices are believed to contain C-14 in: (a) the compound form, such as carbides (e.g., UC or UC<sub>2</sub>) or oxycarbides (e.g., UC<sub>1-x</sub>O<sub>x</sub>, x<1); or (b) the elemental form (10). The compound and the elemental form are likely to come from the transmutation of nitride (e.g., UN) and of dissolved nitrogen, respectively. We believe that the presence of both forms (a) and (b) needs to be confirmed. Up to now, the compounds have not been detected nor characterized successfully: coarse particles have not been detected under the optical microscope; fine particles have not been detected under the transmission electron microscope. The formation of certain compounds can be predictable from modeling exercises, as for instance, from carbide oxidation kinetics (for the reaction of UC to UC<sub>1-x</sub>O<sub>x</sub>, UC<sub>2</sub>, UO<sub>2</sub>, and/or CO) in 10<sup>-4</sup> torr of oxygen partial pressure at 900 and 950° C (21), weight gain (mg/cm<sup>2</sup>) is approximately  $4 \times 10^{23} (\text{mg/cm}^2\text{-hour}) \times e^{-125.5 (\text{kcal/mol}) / (RT)} \times t (\text{hours})$ . From this

relationship and the conversion of the weight gain to the carbide weight (21), approximately 70 % of carbides of  $10^{-3}$  to  $10^{-2}$  cm of thickness and more than 90 % of carbide of  $10^{-6}$  to  $10^{-5}$  cm may have oxidized during reactor operation at 500 to 1800° C. The fuel temperatures during reactor operation are approximately 1800° C at the center and 500° C at the edge (22). Radiation and higher oxygen partial pressures are expected to facilitate the reaction. On the other hand, (a) absorption of oxygen by cladding or (b) larger size of oxidized molecules (e.g.,  $^{14}\text{CO}$  or  $^{14}\text{CO}_2$ ) in SF matrices may make the oxidation of compounds difficult. There are further uncertainties because this equation of the compound oxidation kinetics does not provide kinetic information for the complete conversion of carbides to C (or CO or  $\text{CO}_2$ ).

Besides the formation of these compounds (of carbides or oxycarbides) by transmutation reactions, other mechanisms for the compound formation are less likely to operate during reactor operation. This is because carbide formation rates (23) are slower by many orders of magnitude than carbide oxidation rates in reactors. If present, carbides or oxycarbides may be distributed uniformly, because nitrides from fuel processing appear to be distributed uniformly (24). Still, we do not know the details about the distribution. For instance, nitride formation is only possible thermodynamically in the presence of C-12 (24). More C-12 may be preferentially present near grain boundaries. The potential presence of elemental C-14 may also need to be confirmed. This is because the elemental carbon has been inferred from the high-temperature behavior of carbon-12 (25,26) that is primarily present at grain boundaries. Finally, the inhomogeneous C-14 distribution may also arise from the temperature gradient of the fuel during reactor operation.

C-14 transport in SF matrices is very difficult to assess at lower temperatures. As a basis for this assessment, we first examined available data on diffusivities of fission gases, primarily from reactor experience. Most diffusion data on fission gases in unoxidized SF matrices are available at above 800° C (27-29). If the data are extrapolated to lower temperatures, the diffusion would be unmeasurable under repository conditions. This is mainly because mobility of these gases depends on the formation of accommodating defects whose formation energies are high (30-33). However, if other fast-diffusion mechanisms operate at lower temperatures, this postulate may not be valid. For instance, impurities, dislocations, or clusters may increase the lower temperature diffusion; radiation effects may be significant (31). If  $^{14}\text{CO}$  or  $^{14}\text{CO}_2$  molecules form in the SF matrix, we expect that their mobility is similar to that of fission gases, because of similarly large sizes.

The diffusivity of elemental or dissolved C-14 has not been measured yet in unoxidized or oxidized SF (or  $\text{UO}_2$ ) matrices. Nitrogen diffusivity may approximate C-14 diffusivity because of similar atomic weight (consequently similar atomic radius) (34). However, if nitrogen diffusivities measured in  $\text{UO}_2$  at 1000 to 1600° C (24) are extrapolated to anticipated repository temperatures, they would result in insignificant C-14 releases, unless other fast-diffusion mechanisms operate at lower temperatures. If C-14 behaves more like lighter elements, such as helium or oxygen, its mobility can increase.

As an example, we evaluate below the oxidation kinetics of LWR SF matrices, because the oxygen diffusion in SF matrices controls oxidation kinetics at 175 to 195° C (35). The oxidation kinetics of the sphere model for a single grain is (36)

$$\frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \left( \frac{1}{n^2} \exp\left(-\frac{D n^2 \pi^2 t}{r^2}\right) \right), \quad [1]$$

where "M<sub>t</sub>" and "M<sub>∞</sub>" are the total amounts of diffusing species such as mobile oxygen ions at time "t" and at an infinite time, respectively; "D" is matrix diffusivity of diffusing species; and "r" is the sphere radius. The sphere model or its derivative (37) is a reasonable approximation, at repository temperatures, at which the matrix diffusion is rate-limiting (35,37,38). Then, we obtain the time to complete the oxidation of SF matrices by the relation of (D t / r<sup>2</sup>) approximately equal to 1 (36). This relation is very likely to represent the experimentally determined time to complete oxidation of SF matrices at 175 to 195° C, as given by (35)

$$t_{2.4} \text{ (year)} = 2.97 \times 10^{-13} \exp(26.6 \text{ (kcal/mol)} / (R T)), \quad [2]$$

where t<sub>2.4</sub> is the time (in years) for the complete UO<sub>2</sub> oxidation to UO<sub>2.4</sub>. Table 1 summarizes calculated t<sub>2.4</sub> values at various temperatures. The oxidation will be complete within 10,000 years, at approximately 73.5° C. Consequently, all C-14 inventory will be diffused out of the SF matrix, if C-14 diffusivity is similar to oxygen diffusivity. If other fast-diffusion mechanisms operate at 73.5° C, oxidation time may further decrease. However, oxygen diffusivities in UO<sub>2+x</sub> decrease by many orders of magnitude, as the oxygen to uranium [O/U] ratio becomes closer to the perfect stoichiometry of 2 (30). Therefore, it is difficult to postulate that the results of this sample calculation really represent the kinetics of C-14 diffusion. Nevertheless, diffusivities of oxygen and carbon in UO<sub>2</sub> are considered closer to each other at about 700° C (39). This suggests that diffusivities of oxygen and carbon in SF can be similar under repository conditions unless governing mechanisms change at lower temperatures.

Nonstoichiometric oxides are generally known to show faster diffusivities; nevertheless, the mobility of remaining C-14, upon UO<sub>2</sub> oxidation to UO<sub>2.4</sub>, is not well-understood. In higher oxides (i.e., [O/U] greater than 2.4) such as U<sub>3</sub>O<sub>8</sub>, the situation becomes more complicated as the SF matrix becomes powdered (40). Also, radiation damage makes U<sub>4</sub>O<sub>9</sub> and U<sub>3</sub>O<sub>8</sub> amorphous (41,42). The amorphous phase can increase C-14 mobility significantly. Still, we do not know the extent of recovery or decomposition of the formed amorphous phases under repository conditions. If C-14 is bound to excess oxygen (such as <sup>14</sup>CO<sub>2</sub> formation) during conversion to UO<sub>2.4</sub> or higher oxides, C-14 mobility may become less significant because of its large size. It may become significant only when: (a) grain sizes become smaller either from high-burnup (18) or from oxidation (43,44); or (b) amorphous phase or dislocation networks exist. Alternatively, UO<sub>2</sub> oxidation may help release bound C-14 to residual oxygen produced during irradiation. The available diffusivities in the above cases are so uncertain that we need to directly confirm the above postulates about C-14 transport.

If the amounts of carbides or oxycarbides are significant, C-14 releases would be very restricted from their slow oxidation kinetics, based on high-temperature oxidation data (21). However, C-14 may be released significantly from these compounds if: (a) radiation facilitates oxidation of these compounds; and (b) other fast-oxidation mechanisms operate at lower temperatures. Dissolved C-14 (associated with various defects) may be less mobile in SF matrices compared with elemental C-14, from energetics consideration in solid-state diffusion.

Data on C-14 releases during the oxidation of SF matrices have been obtained only at much higher temperatures than the anticipated repository temperatures. Roasting LWR SF in air at 480° C released approximately 50 % of the C-14 in 3 to 4 hours (45); and voloxidation of LWR SF to  $U_3O_8$  at 490° C in air released approximately 20 % of the C-14, in approximately 6 hours (46). It is likely that these large amounts of C-14 releases are related to  $U_3O_8$  formation. As an example, the release kinetics of Kr-85 is akin to the oxidation kinetics of  $UO_2$  to  $U_3O_8$ . This was noted for British irradiated  $UO_2$  in air at 400° C (47), and for LWR SF during voloxidation at 490° C (46). Also, it has been recognized that fission gas releases are related to  $U_3O_8$  formation during reactor operation (48). The likely mechanisms for the C-14 release kinetics, during roasting or voloxidation, involve the aforementioned faster C-14 diffusion, upon being subjected to high temperatures. If we evaluate Eq. [2] at temperatures of these tests, all C-14 should have been released. Therefore, there are many possibilities for the fractional C-14 release from roasting or voloxidation of SF. For instance, C-14 diffusivity may be much smaller than oxygen diffusivity; significant amounts of carbides or oxycarbides may be present; or gaseous  $^{14}CO_2$  or  $^{14}CO$  may form or be present. In any of these cases, it appears that the powdering of SF matrices during oxidation plays an important role in C-14 releases at these temperatures. (Alternatively, the significant rim effects may be another important factor in high-burnup SF).

We will consider the powdering of SF matrices on the higher oxide formation and its effects on C-14 releases. We will adopt a portion (approximately 4 % (49)) of the elastic strain energy associated with volume expansion (approximately 35.6 % (43)) upon higher oxidation, to create new surface areas of formed particles. Then, from energy balance, the average size of assumed spherical particles would be approximately  $10^{-6}$  cm (without taking into account grain boundaries). This is the observed size of  $10^{-6}$  to  $10^{-4}$  cm of  $U_3O_8$  in  $UO_2$  or SF oxidation (43-45). From powdering, it is expected that: (a) small particles release C-14 (or its molecules) faster in a shorter diffusion distance; (b) C-14 is detached faster on a large surface area by forming  $^{14}CO_2$ ,  $^{14}CO$ , or  $^{14}CH_4$ ; or (c) C-14 is detached faster on a large internal surface area (e.g., intergranular cracks). Unfortunately, it is difficult to relate these high-temperature characteristics to C-14 releases at repository temperatures. At repository temperatures: (a) C-14 diffusion in higher oxides may be slower than that in lower oxides, if inferred from the extrapolated kinetics of  $U_3O_8$  formation (50,51); and (b) higher oxides may not form.

From the aforementioned discussion, we have found that  $UO_2$  oxidation may play an important role in long-term C-14 releases. Therefore, we will summarize

our view of  $UO_2$  oxidation to  $UO_{2.4}$ , or to higher oxides. As implied by the data in Table 1, the oxidation of SF matrices is likely to be complete within a period of 10,000 years at temperatures above approximately  $73.5^\circ C$ . However, there are significant uncertainties about the results, primarily arising from uncertainties associated with activation energies for oxidation (35,38). Additionally, the potential change of oxidation mechanisms at lower temperatures is not known. Nevertheless, as suggested in Table 1, for (a) the high thermal load ACD or SCP design and (b) early container failure for any design, oxidation to  $UO_{2.4}$  is likely to be complete in a short period.

Studies of both SF matrices and  $UO_2$  have shown the times to initiate higher oxide formation (i.e., induction period to reach  $[O/U]$  equal to 2.4 in Eq.[2]) (35). Besides this induction period, a time-delay " $\delta$ " was observed in SF at approximately  $250^\circ C$ , maintaining a plateau of  $[O/U]$  equal to 2.4 over time. Whereas induction times at various temperatures follow the Arrhenius relation, the time delay shows a peculiar behavior. No accurate measurement of  $\delta$  values could be made because  $\delta$  values were too short above  $283^\circ C$  and too long below  $225^\circ C$ . It is believed that the investigation of this time delay is an important topic for future research.

The higher oxide formation can be hindered kinetically below a threshold temperature. The long incubation period (or the large energy barrier) for the higher oxide nucleation may be responsible for such behavior. However, there are many uncertainties about the long  $\delta$  values. For instance, if amorphous higher oxides are present along grain boundaries at  $[O/U]$  less than 2.4,  $\delta$  values would be short. Our view on  $\delta$  will be presented in another paper.

Data on  $UO_2$  oxidation (50,51) suggest that the  $U_3O_8$  growth kinetics can be slower than the  $UO_{2.4}$  growth kinetics at the repository temperatures. This is from the extrapolation of high-temperature kinetics to repository temperatures at which  $U_3O_8$  is not normally observed. Also, the strain energy associated with the  $U_3O_8$  formation can be accommodated, without the powdering of SF matrices, if the amount of  $U_3O_8$  formed is not significant. Nevertheless, we should note that aqueous conditions can exist, in Yucca Mountain, in which the higher oxide formation will be facilitated at lower temperatures (52,53).

Summarizing this subsection, under dry conditions the formation of higher oxides may lead to significant C-14 releases; however, there are uncertainties about the extent of this higher oxidation within the SF matrix and about C-14 diffusivity in higher oxides at lower temperatures. Similarly, it is unclear whether there will be significant C-14 releases from lower oxidation to  $UO_{2.4}$ , or from unoxidized SF matrices, because: (a) the existence or the stability of various C-14 forms in the SF matrix (i.e., carbides or oxycarbides, elemental C-14, and gaseous molecules of the C-14) has not been confirmed; and (b) uncertainties about C-14 diffusivity are significant.

### 2.1.2 Cladding

Cladding is also a source of C-14 that was activated during reactor operation (10). We discuss only Zircaloy, because it is most widely used for cladding. We assume homogeneous C-14 distribution based on the observed C-14 releases from the cladding matrix (54). Van Konyenburg's work (8,10) postulates that

C-14 is present as: (a) carbides (e.g., ZrC) or similar compounds (e.g., Zr(C,N,O)<sub>x</sub>); and (b) dissolved ions. As for C-14 of SF matrices, this postulate needs experimental confirmation. Dissolved ionic C-14 may be attracted to various defects or oxygen to accommodate strain or for charge neutrality. Kopp and Münzel (55) conducted C-14 release experiments of Zircaloy-2 doped with C-14 by annealing at approximately 730° C, with prior homogenization at 700° C. In their experiments, C-14 releases were rapid (10 to 80 % in approximately 200 hours) at 200 to 600° C, in argon, with 5 vppm of O<sub>2</sub> and H<sub>2</sub>O. The C-14 release followed a parabolic kinetics. Based on this observation, Kopp and Münzel postulated that C-14 was distributed quite uniformly in the grain matrix of cladding and C-14 diffused to the surface.

Over long time periods in a repository, it is not certain whether the oxidation of cladding will decompose carbides or similar compounds, if present, unless: (a) radiation facilitates the decomposition; or (b) oxidation increases the surface area significantly. For instance, intact carbides were observed in steam corrosion of Zircaloy-2 at 300° C and atmospheric pressure (56). Kopp and Münzel did not consider <sup>14</sup>CO or <sup>14</sup>CO<sub>2</sub> formation in their work, possibly because of its great formation energy in cladding matrices. Nevertheless, they observed the strong affinity of C-14 to oxygen along grain boundaries. Therefore, as in the bare SF, we cannot rule out the presence of <sup>14</sup>CO or <sup>14</sup>CO<sub>2</sub> associated with various defects.

Before discussing the effects of oxidation on C-14 mobility, we should address C-14 diffusion in unoxidized cladding. The diffusivity data of Zircaloy-2 by Kopp and Münzel (55) agree with other data in the literature regarding carbon diffusivity in Zircaloy-2 (27,34). We choose these diffusivities for both Zircaloy-2 and Zircaloy-4 because these two alloys are similar in chemical compositions and structures. Then, we assess C-14 releases by calculating  $(Dt)^{1/2}$ . Total C-14 will be released at  $(Dt)^{1/2} \sim$  grain radius,  $r$  (see page 7). These values of  $(Dt)^{1/2}$  for 10,000 years will be approximately 0.4  $\mu\text{m}$  at 200° C (for  $D$  equals  $5.1 \times 10^{-21}$  cm<sup>2</sup>/second) and approximately 0.04  $\mu\text{m}$  at 150° C (for  $D$  equals  $4.4 \times 10^{-23}$  cm<sup>2</sup>/second). Considering: (a) grain size greater than approximately 10  $\mu\text{m}$  (57); and (b) C-14 inventory in Zircaloy, significant C-14 diffusion is unlikely in unoxidized cladding under repository conditions. C-14 may diffuse faster in oxidized Zircaloy than in unoxidized Zircaloy. This is an inference from available diffusion data on (a) carbon in zirconium and (b) self-diffusivities in zirconium and ZrO<sub>2</sub> (mainly oxygen) (27,58,59). If carbon diffusivity in ZrO<sub>2</sub> increases as much as ZrO<sub>2</sub> self-diffusivity increases, the C-14 diffusivity in ZrO<sub>2</sub> may become significant. Uncertainties concerning self-diffusivities of ZrO<sub>2</sub> are so great (59), however, that this postulate of significant diffusion represents only the worst case.

Two independent databases are available to evaluate C-14 releases from LWR SF cladding: (a) Van Konynenburg obtained C-14 release data from SF assemblies at 275° C (11), and the release was considered to have come mainly from cladding; and (b) Smith and Baldwin showed significant C-14 releases from cladding annealed at 100 to 350° C (54). Smith and Baldwin claimed that C-14 was released from the Zircaloy-4 oxide formed during reactor operation. They analyzed their data with C-14 diffusion through a finite thickness plane of the formed oxide. They further suggested that the porous structure of

post-transition oxide is related to C-14 releases; that potential rate-limiting steps include diffusion, desorption, or detrapping.

The zirconium oxide that Smith and Baldwin tested had formed during reactor operation. They attributed the thick (8 to 20  $\mu\text{m}$ ) oxide to porous unprotective post-transition oxide, and the thin (3 to 8  $\mu\text{m}$ ) oxide to compact protective pre-transition oxide. The typical temperature of cladding during reactor operation is approximately 350° C for approximately 3 years (22). Under this condition, formulas that Rothman summarized (60) (see Table 2) give approximately 3.5  $\mu\text{m}$  of pre-transition oxide in the presence of radiation (61). Therefore, both thick and thin oxides used by Smith and Baldwin were likely to have porous post-transition oxide in a significant amount. Some of their data show that C-14 releases from the thin oxide is faster than that from the thick oxide; this is contrary to their postulates of faster C-14 releases in the thick oxide. Also, the C-14 release behavior in air and in argon was significantly different for the same formed oxide. The difference suggests that the surface reaction of C-14 to  $^{14}\text{CO}_2$  released C-14 that had diffused to surfaces from both the oxide and the metal. Therefore, besides their proposed structural transformation as the oxide grows, the large surface areas of the porous structure appear to be related to the observed C-14 release. If  $^{14}\text{CO}_2$  forms or C-14 is associated with oxygen in the cladding matrix, C-14 can be released by debonding oxygen from C-14, during the oxidation. Even if it is not dissociated from oxygen,  $^{14}\text{CO}_2$  can still be released on a large surface area of porous  $\text{ZrO}_2$ .

In Smith and Baldwin's analyses (54), total C-14 releases are inversely proportional to the extracted C-14 diffusivities from their model. When the calculations are extrapolated to 10,000 years at 100 to 200° C, the total C-14 is expected to be released from the oxide layer. We believe that a sphere model (36) or a model of a thinner plane appears to be a better choice, because the oxide formed during reactor operation has micropores and cracks (62). With these new models, it is likely that the total C-14 is released in the formed oxide, within 10,000 years, at 100 to 200° C, regardless of the overall oxide thickness. This is because micropores and cracks provide shorter diffusion distances. However, other mechanisms may lead to C-14 retention in the oxide. Such mechanisms include the slow carbide oxidation. Also, Smith and Baldwin data appear to follow time laws of the inverse of n-th power ( $t^{1/n}$ ). If we extrapolate their data to 10,000 years, total C-14 may not be released for values of n greater than 3, at 100 to 200° C.

As in SF matrices, we consider that Zircaloy oxidation is primarily related to C-14 releases from cladding. From the database on Zircaloy (Zircaloy-2 and Zircaloy-4) oxidation kinetics at 232 to approximately 400° C (60), various thicknesses of cladding subjected to oxidation is calculated at 100, 150, and 200° C, in Table 2. The oxidation is unlikely to be significant in the nominal cladding thickness of approximately 0.61 mm (54), unless other fast-diffusion mechanisms operate at lower temperatures. For instance, at lower temperatures, individual grains may oxidize after preferential oxidation of grain boundaries (instead of uniform surface oxidation). In this case, a significant oxidation may occur under the worst circumstance, considering the results in Table 2 (and our unpublished results at varying temperatures). However, a threshold temperature may exist for the formation of

post-transition oxides. The post-transition oxidation may be delayed below the threshold temperature. For instance, Kass obtained only pre-transition oxides at 232 to 316° C in degassed deionized water (63). Concluding this subsection, it is unlikely that C-14 will be released significantly from unoxidized or oxidized Zircaloy under dry conditions (unless effects of radiation, impurities, defects, or grain boundaries are significant), because of (a) low C-14 diffusivity in unoxidized Zircaloy, and (b) slow Zircaloy oxidation.

## 2.2. Release from Spent Fuel Matrices and Cladding under the Aqueous Dissolution Condition

It was necessary to establish a reference source of water at the disposal site in order to conduct experiments and analyses of waste package dissolution. The well chosen to characterize the water flowing through the Topopah Spring Member at the Yucca Mountain repository was number J-13. Under actual repository conditions, SF may dissolve in the groundwater either under near-static immersion conditions or under drip conditions. (High flow conditions are not considered in this paper). The heat of emplaced waste packages may concentrate the dissolved species of this groundwater (64), and radiolysis may also alter its chemistry.

We will primarily discuss C-14 releases from unaged bare SF in the J-13 well water. The C-14 release from passive layers formed during aqueous general corrosion of cladding appears to be essentially the same as that from oxides formed in dry environments. Zircaloy oxidation to pre-transition oxides is the same in water, steam, or air, at 350° C (57). If passivity breaks down, by localized corrosion, the C-14 release from cladding could be more rapid because of the faster Zircaloy dissolution. We will discuss Zircaloy susceptibility to faster dissolution in Section 3.

Wilson conducted long-term semi-static immersion tests of LWR SF in the J-13 well water at 25 and 85° C, for extended periods of over 200 days (15,65). The magnitude of the C-14 released in a closed test vessel suggested that: C-14 was released preferentially from grain boundaries; and some C-14 was likely to precipitate as carbonate phases (15). The carbonate phases are considered to have formed mainly from bicarbonate ions in J-13 well water. However, in an open test vessel at 25° C, C-14 releases could not be measured (65). This was attributed to the fact that most of the C-14 released in the open system was lost to the atmosphere as  $^{14}\text{CO}_2$ . Measurements of C-14 releases at 85° C under immersion conditions in the open system were not made. Under drip conditions of J-13 well water at 90° C, Argonne National Laboratory reported carbon-calcium-bearing phases as colloid form in SF tests for approximately 120 days (66) but not in  $\text{UO}_2$  tests for a longer period of over 200 weeks (53). Detailed explanations of these observations have not been made. C-14 fixation in calcium-bearing phases has been examined extensively in C-14 waste management (67)). At higher temperatures, the calcite fixation of C-14 may be possible; however the fixation could be reversed as temperatures drop (68). This would be especially true at a low pH region, e.g., one resulting from radiolysis under an aqueous film on SF surfaces (66).

Current long-term performance assessments assume conservatively that C-14 is released at the dissolution rate of SF matrices after instantaneous releases

(69,70). The dissolution rates of SF matrices can be represented, in turn, by the alteration rates (i.e., the precipitation rates on SF surfaces), the precipitation rates on test vessel surfaces, and the convection rates (by groundwater flow), of dissolved uranium ions. Then, the question is whether the dissolution rate is constant or decreases with time. This is an important question. If dissolution proceeds linearly with time, a significant portion of the total C-14 inventory can be released from SF matrices over a geological period. On the other hand, if a non-linear time law such as parabolic law governs, a significant C-14 retention may be obtained over the geological period. In this section, we summarize the recent understanding of dissolution mechanisms of SF matrices and discuss the role of the altered layer in the dissolution of SF matrices. We assume carbides or oxycarbides, if present, will also dissolve in groundwater.

Gray determined the dissolution rates of LWR SF matrices in the J-13 well water at 25° C, by comparing the release rates of Cs-137, Sr-90, and Tc-99 from flow-through tests with those from immersion tests (71). His analyses suggest that the SF matrix may dissolve linearly with time. However, we have found that some data show that solubility limits of Cs-137 and Sr-90 may have been reached in immersion tests of bare SF matrices in the J-13 well water at 25 and 85° C (15). Also, Tc-99 data from the immersion tests had uncertainties associated with dissolution of fine intermetallic particles (15). Additionally, radiolysis effects may differ in immersion tests and flow-through tests. Therefore, we attempt, below, to analyze the uranium in the precipitated materials (on SF surfaces and test-vessel walls) and convected uranium from leachate replenishments, to determine the dissolution rates of SF matrices in the J-13 well water at 25 and 85° C. The analysis of the uranium data is still a confirmatory practice of the analysis of fission product data, because of large errors involved in the uranium databases. Besides the uncertain radiolysis effects, the errors also arise from undissolved fuel grains, in the analysis of the altered layer (15). The analyzed altered layer could have been comprised of undissolved fuel grains from the stripping process of the altered layer on the SF surfaces. Because of these uncertainties, we also need to discuss the role of the altered layer on the SF surfaces, in the dissolution of SF matrices, more qualitatively, to support the hypothesis made from elemental release data.

During the dissolution of SF in oxidizing J-13 well water, the SF matrix dissolves in leachates and forms an altered layer on the SF surfaces. Before SF is under aqueous dissolution conditions, it could have been oxidized previously, under dry conditions. The altered layer comprises uranyl oxide hydrates (such as schoepite) as intermediate phases and various uranyl silicates (such as uranophane) as final solubility limiting phases (15,53). The altered layer formed on the SF surface is unlikely to protect against continuous matrix dissolution, in oxidizing HLW repositories. The unprotective nature may arise from: (a) displacement damages of alpha particles (72) or radiolysis effects (73) (although radiation energy may be absorbed in the altered layer, partly); (b) stress generation during the formation of the altered layer, oxidation, or gas (such as helium) buildup; and (c) microbial activities (74). Moreover, the altered layer may have, inherently, micropores and intracrystalline spaces. Larger (than an atom) continuous spaces within the altered layer are presumably necessary for the mass transport required for the continuous matrix dissolution. Variations in

environmental conditions can also lead to the instability of the altered layer. Wet-dry cycles under drip conditions of groundwater may vary the chemistry of groundwater, subsequently leading to dryout, redissolution, or spall-off of the altered layer. Occluded areas can also vary the chemistry of groundwater. Also, any disturbance caused by external stress waves such as seismic events may destroy the altered layer.

Electrochemical studies demonstrated the irreversible dissolution of  $UO_2$  in various solutions at room temperature (75,76); they further suggested that the altered layer may not be protective in carbonate solutions at room temperature (77).  $UO_2$  tests in deionized water at 75° C showed that the altered layer was nearly absent despite precipitated materials formed in leachates (73). SF tests in the J-13 well water at near room temperature did not show stable altered phases on the SF surfaces (15,65). Also, in dripping J-13 well water at 90° C, the altered layer was found offset from the dissolving  $UO_2$  surface (53). Other possible indications of the instability of the altered layer may include cyclic behavior of leachate concentration in semi-static tests of SF, for periods up to more than 2 years, at both room temperature and 85° C (78). Leachate supersaturation, formation of protective layer, and loss of protection could have been repeated, to cause the cyclic behavior of the leachate concentration.

We deduce, from these observations, that precipitation may continue in oxidizing aqueous environments during the long-term repository performance of SF. Then, all the above inference leads primarily to a linear time law as the alteration kinetics; however, we also need to consider a non-linear time law, if the dissolution involves any unknown processes. For instance, the dissolution may be limited by (aqueous or solid-state) diffusion; surface area may change as time elapses. We evaluate the linear time law, first, based on mechanistic understandings, and then the non-linear time law, by a phenomenological approach. The linear time law assumes that a long-term steady state exists.

For a specific element, the dissolution rate of the dissolving phase under oxidizing conditions may be approximated in the simplest form by (76)

$$R_{dis} = S k_e f(E), \quad [3]$$

or by

$$R_{dis} = S K_{\infty} (1 - Q/K), \quad [4]$$

where "S" is the surface area of the dissolving phase, " $k_e$ " is the rate constant for electrochemical dissolution, " $f(E)$ " is the dependence of the dissolution rate on the electrochemical potential "E," "k" is the rate constant for the chemical dissolution, "Q" is the product of constituent activities to the power of corresponding stoichiometries in solutions, and "K" is the equivalent equilibrium values of Q.

Eq.[3] represents electrochemical dissolution, and Eq.[4] represents solubility-controlled dissolution. In the near-static environments of our

primary concern, we may not neglect solubility-controlled dissolution under supersaturated conditions with respect to the altered phase. In the steady state, the value of E (or Q) is nearly constant (i.e., the dissolution rate is constant) in Eq.[3] and Eq.[4]. This leads to the linear time law. We will evaluate these equations with existing data on uranium releases from flow-through tests and from immersion tests by Pacific Northwest Laboratory in the J-13 well water (15). We also consider electrochemical test results by Atomic Energy of Canada, Limited in chloride solutions (75,76), for the purpose of a relative comparison. Table 3 presents data for terms in Eqs.[3] and [4].

In Table 3, we compare dissolution rates from flow-through tests (or electrochemical tests) with rates of precipitation and convection from immersion tests. Two dissolution rates in J-13 well water at 25 and 85° C appear to be close to each other within a narrow error band. Gray showed that the dissolution rates in flow-through tests decreased initially, and then appeared to reach steady-state (constant) values as time elapses (71). The transient times to reach the apparent steady state appeared to be short. His apparent steady-state values are used in Table 3. The comparison made in Table 3 suggests that the SF matrix may dissolve linearly with time. (Immersion test results may be a little higher than flow-through test results. Perhaps, groundwater radiolysis is responsible for this discrepancy.) Flow-through test results with the J-13 well water at 85° C are not available. Therefore, values measured in two different carbonate/bicarbonate solutions are given in Table 3, for an indirect comparison.

Using a constant dissolution rate in Table 3, and approximately 10 g/cm<sup>3</sup> of SF density (15), the SF matrix of approximately 0.03 mm at 25° C and approximately 0.2 mm at 85° C of the SF matrix will dissolve within 10,000 years. If each grain is exposed and dissolved, the radionuclide release will be facilitated because of the small size of each grain. For instance, Wilson suggested intergranular attack near SF surfaces (15,78). If SF is subjected to groundwater drip conditions, the groundwater chemistry in an aqueous film on SF surfaces may be altered (64,66). Additionally, the role of backfill, in the alteration of groundwater chemistry, is largely unknown. Considering that: (a) the average size of SF particles is in the order of mm (15,79); (b) the average grain size is in the order of 10 μm (35,79); (c) the regulatory limit of C-14, 0.1 Ci/MTHM (3); and total inventory of C-14 in the SF matrix, 0.53 Ci/MTHM (8-11), the aforementioned 0.2 mm dissolution of the SF matrix can be significant.

Contrary to the aforementioned postulate of linear time law, there is a possibility that non-linear time law may govern the SF matrix dissolution in a geological period. For the aforementioned postulate of linear time law, the amount of precipitated uranium determined in immersion tests has appeared to be the same as that of uranium dissolved in flow-through tests. However, there are uncertainties about the amount of precipitated materials. For example, the analyzed precipitated materials could have been comprised of undissolved fuel grains from the stripping process of the altered layer on the SF surfaces (15). The real amount of precipitated materials could have been smaller. Similar arguments can be made for radiolysis effects. Then, the dissolution of SF matrices could have slowed down gradually as the altered layer became an effective (aqueous or solid-state) diffusion barrier as time

elapses. In the presence of diffusion barriers, radionuclide releases are likely to slow down significantly, during long-term SF performance.

Because detailed mechanisms for diffusion-barriers effectiveness are not well-understood, we present a phenomenological description of the diffusion-limited kinetics of the SF matrix dissolution, as

$$R_{dis,d} = k S (t+a)^{-\frac{1}{n}}, \quad [5]$$

where "S" and "t" represent surface area of the dissolving phase and time respectively; "k," "a," and "n" are constants; and n is an integer. In many problems of diffusion-limited kinetics, we expect n=2; however, the various geometries involved are likely to result in other n values too. For instance, precipitated materials on SF surfaces may vary the surface "S" in a time-dependent manner. This will lead to the effective n value other than 2 (for example, n=3 or 1). Assuming that Eq.[5] represents the dissolution rates of SF matrices, we conducted a sample calculation for the long-term dissolution of the SF matrix. We took the transient data of flow-through tests (71) showing a gradual decrease of the dissolution rates of SF matrices. Fitting the transient data to Eq.[5] with n=2 determined "k" and "a" values. The numerically determined Eq.[5] was extrapolated to a geological period. The extrapolated values of the amount of the dissolved SF matrix were far less (by many orders of magnitude) than those from the linear time law, Eq.[3] or Eq.[4]. Similar conclusions can be drawn if we extrapolate the data of gradually decreased releases of Sr-90 from immersion tests of LWR SF in Swedish groundwater (80).

From the assessments made in this section, we conclude that C-14 releases from SF matrices, under aqueous dissolution conditions, can be significant. This is mainly because the altered layer does not necessarily inhibit SF matrix dissolution. C-14 releases from aqueous general corrosion of cladding will be similar to those under dry conditions, or C-14 releases may be more significant from localized corrosion. In the next section, we will summarize the role of the container in the assessment of the C-14 source term.

### 3. RELEASE FROM CONTAINER FAILURE

We will discuss cladding as another type of container, during our discussion on containers. This is because both cladding and containers encase SF matrices, and their degradation modes are similar. The container's role in C-14 releases will be either total containment of the C-14 inventory inside containers, or gradual C-14 releases from failed containers. Therefore, the first question is whether the container integrity is preserved for an extended period. The second question is how failed containers can modify C-14 release modes. We will summarize what is known about these two questions (the second question and then the first question), vis-à-vis the Yucca Mountain environments.

Zwahlen, Pigford, Chambre, and Lee (12) and Pescatore and Sullivan (13,14) postulate that small perforations in containers will delay  $^{14}\text{CO}_2$  releases from waste packages. Small perforations modify the flux of mass transport. This original postulate has been made for one perforation, but the postulate is considered valid for many perforations. Pitting corrosion is the most likely failure mode that will result in small perforations. On the other hand, other failure modes are likely to lead to either catastrophic failure or general corrosion. It is expected that pitting corrosion takes place only at below an estimated maximum temperature of approximately  $120^\circ\text{C}$  and at sufficient relative humidity for aqueous film formation (or under immersion conditions) (7,81). Three regimes of corrosion potential, "E," have been considered to categorize the pitting behavior (82):

- (a) Nucleation and growth of pits occur if E is greater than  $E_p$ ;
- (b) Arrest of growing pits occurs if E is less than  $E_{rp}$ ;
- (c) Growth of existing pits occurs if E is greater than  $E_{rp}$  and less than  $E_p$ ;

where " $E_p$ " and " $E_{rp}$ " are the pitting potential and the repassivation (or protection) potential, respectively. Presently, we are primarily concerned with the formation of a limited number of small pits penetrating through the container walls. In the case of (a), the  $^{14}\text{CO}_2$  release may not be delayed because of fast degradation of containers. For the effective delay of  $^{14}\text{CO}_2$  releases, the following conditions should be obtained: case (a) followed by case (b) or case (c).

Very little is known about the size, depth, and distribution of pits generated for current candidate container materials or cladding in the Yucca Mountain environments. It is generally known that smaller-in-diameter, but deeper, pits develop in more passive materials. Unlike highly passive container materials or cladding, carbon steels normally show much larger diameters, but more shallow pits. Also, the pit factor (i.e., ratio of pit penetration to uniform penetration) is much smaller, about 2 to 4, for carbon steels (81).

A few data available (83,84) show that the pit size is in the order of  $\mu\text{m}$  to the order of mm (except in the order of cm observed in soil environments (85)); and the pit density is approximately 0.1 to 100 / $\text{cm}^2$  in most aqueous environments. The Figure shows typical examples of size and distribution of pits. Although site-specific and material-specific data on pit morphology are not available, we expect that a limited number of small pits lead to controlled C-14 releases because the aforementioned measured sizes and distributions are comparable with those used in the modeling, partly (12-14). The detailed comparison will not be presented here. It involves transport mechanisms (such as gaseous diffusion of C-14), the conversion of sizes of many pits to the size of an effective pit, corrosion products within the pits, and the surface area of the cladding or the container.

The scenario for the development of through-wall pits may be as follows for a representative case of a container having a corrosion allowance outer layer and a corrosion-resistant inner layer. During the breach of the outer layer by many failure modes, C-14 will not be released. Until the first pit (or crack) penetrates through the outer layer, the container will degrade at the

pitting (or crack growth) rate of the outer layer. As pits (or cracks) reach the inner layer, the remaining outer layer will corrode more rapidly, because of large galvanic currents. During this period, the sacrificial outer layer will help prevent pit initiation in the inner layer. Then, the remaining concern is whether pits form in the passive inner layer or cladding, leading to modifying C-14 releases from the SF matrix. The through-wall pits in the inner layer or cladding are not expected to broaden extensively, because of repassivation or polarization, until pit coalescence takes place. Therefore, through-wall pits formed in the inner layer or cladding are likely to delay C-14 releases. Unfortunately, at present, the nature of the repository conditions that may lead to the formation of only a limited number of small through-wall pits is not well understood for candidate container materials or for cladding. Hence, quantitative assessments of C-14 releases by through-wall pits cannot be made at present.

Failure modes other than pitting include:

- (a) Oxidation, mechanical failure, and materials alteration under dry conditions; and
- (b) Crevice corrosion, stress-corrosion cracking, hydrogen embrittlement, and mechanical failure under the condition of aqueous degradation.

Under dry conditions, oxidation rates are very slow: about 0.002 to 0.1  $\mu\text{m}/\text{year}$  from extrapolations from high temperature data (7). Unless there is sufficient relative humidity for aqueous film formation for atmospheric corrosion, the oxidation rate is very slow. However, one area that has not been investigated extensively is preferential oxidation of grain boundaries. Preferential oxidation has been observed at high temperatures (86). Preferential oxidation at repository temperatures may also occur, if its kinetics is significant in a geological period. As a simple argument, grain-boundary diffusivities are much faster than matrix diffusivities. Therefore, grain boundary oxidation may not be negligible, under repository conditions. If the formation of grain boundary oxides is hindered kinetically, or other mechanisms operate at repository temperatures, however, grain boundaries may not be attacked.

In mechanical failure, any type of macroscopic failure such as buckling can be considered to lead to container breach. More strictly, microscopic fractures are responsible for the failure. For various stress intensifications, values of fracture toughness have been tabulated in many text books. Under dynamic conditions, fracture toughness will decrease significantly for non-FCC (face centered cubic) structures. Austenitic phases may be transformed to non-FCC structures, either along grain boundaries or in matrices. For instance, a significant decrease of impact strength was observed for sensitized alloy C-4, at 538° C, for 16,000 hours (87).

Materials alteration is also an important degradation mode mainly caused by phase transformation or chemical segregation (such as de-alloying driven by diffusion-induced grain-boundary migration (88)). Materials alteration is likely to accelerate other failure modes, including localized corrosion, stress-corrosion cracking, or mechanical failure. However, even in a geological period, this transformation may be hindered kinetically because

repository temperatures are not high enough to lead to a significant amount of reaction products.

Failure modes unique in aqueous corrosion are pitting corrosion, crevice corrosion, stress-corrosion cracking, and hydrogen embrittlement. We have discussed the consequences of pit propagation previously in the gradual  $^{14}\text{CO}_2$  release. The propagation of other failure modes may not be relevant to the C-14 issue. This is because propagation may be fast; consequently, failure may not lead to gradual C-14 releases. Detailed discussions on propagation are deferred. Then, an important concern in total C-14 containment is the initiation of any of these failure modes.

During long-term repository performance of waste packages, environmental conditions may reach a point where  $E$  is greater than  $E_{rp}$ , so that crevice and pitting corrosion are initiated. Such conditions may include concentrated groundwater on the container (or cladding) surfaces (from drip processes) or in crevice areas, or oxidants formed by radiolysis. For stress-corrosion cracking, the use of the critical potential has not been established yet. If the critical potential can be used, we may make postulates about the initiation of stress-corrosion cracking similar to those made about the initiation of localized corrosion. For these three modes, the sacrificial outer layer will be beneficial, if the sacrificial layer is not consumed rapidly. In hydrogen embrittlement, several sources of hydrogen were identified (89): hydrogen is produced through galvanic coupling, crevice corrosion, microbial activities, and radiolysis. General current understanding about hydrogen embrittlement is that failure rates become severe, gradually, as any of these hydrogen sources increases hydrogen fugacity. In some cases, the use of higher temperatures can help avoid hydrogen embrittlement. For instance, hydrides for embrittlement may not form at higher temperatures in Grade-12 Titanium.

There is also uncertainty about weld effects and microbial corrosion. Weld effects may be understood partly in terms of materials alteration or stress intensification; microbial corrosion may enhance general corrosion rates or susceptibility to localized corrosion. Still, there are other unknown failure modes, such as: (a) radiation-induced hydrogen embrittlement in moist environments; or (b) oxygen embrittlement (90).

In summary, we have discussed qualitatively various factors that govern total C-14 containment inside containers or cladding. C-14 releases can be delayed, even by the formation of small through-wall pits in containers or cladding, when compared with C-14 releases from bare SF.

#### 4. CONCLUSIONS

This paper evaluates the possibility of long-term C-14 releases from moderate-burnup SF of pressurized water reactors and from containers in the anticipated environments of the proposed Yucca Mountain repository. The following conclusions are drawn from arguments, models and/or data presented here:

- (1) Under dry conditions, the higher oxide formation may lead to significant C-14 releases from bare SF; however, there are uncertainties about the extent of the higher oxidation of the SF matrix and about C-14 diffusivity in higher oxides at lower temperatures. Similarly, it is unclear whether there will be significant C-14 releases from lower oxidation to  $UO_{2.4}$  or from unoxidized SF matrices, because: (a) there are not enough confirmation data regarding the existence or the stability of various C-14 forms in the SF matrix (i.e., carbides or oxycarbides, elemental C-14, and gaseous molecules of C-14); and (b) there are significant uncertainties about C-14 diffusivity.
- (2) Under dry conditions, it is unlikely that C-14 will be released significantly from unoxidized or oxidized Zircaloy cladding (unless effects of radiation, impurities, defects, or grain boundaries are significant), because of: (a) low C-14 diffusivity in unoxidized Zircaloy, and (b) slow oxidation of Zircaloy.
- (3) C-14 releases from SF matrices under aqueous dissolution conditions can be significant. This is mainly because the altered layer does not necessarily inhibit SF matrix dissolution. C-14 releases from aqueous general corrosion of cladding will be similar to those under dry conditions, or C-14 releases may be more significant from localized corrosion.
- (4) Besides the evaluation of gradual C-14 releases from SF assemblies, the role of metallic barriers in waste packages has also been assessed. Various factors governing total C-14 containment in containers or cladding have been discussed qualitatively. Also, C-14 releases can be delayed, even by the formation of small through-wall pits in containers or cladding, when compared with C-14 releases from bare SF.

Although we do not have completely definitive information yet, it is clear that the spent fuel matrix, cladding, and containers can serve as important barriers to C-14 releases from the waste packages, in a repository environment.

## 5. ACKNOWLEDGMENTS

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Table 1. Calculated Times to Complete the Oxidation of UO<sub>2</sub> to UO<sub>2.4</sub>

T (° C)	200	150	100	70	50
t <sub>2.4</sub> (years)	4.8x10 <sup>-1</sup>	1.3x10	9.1x10 <sup>2</sup>	2.1x10 <sup>4</sup>	2.3x10 <sup>5</sup>

Table 2. Thicknesses of Cladding Subjected to Oxidation and Transition Time from Pre-Transition Oxide to Post-Transition Oxide

Temperature (° C)	Transition Time (Years)	Thickness Oxidized (cm for 10,000 Years)		
		Pre-Transition and Post-Transition	Post-Transition Only	Cyclic Pre-Transition
100	1.6x10 <sup>5</sup>	2.9x10 <sup>-5</sup>	4.6x10 <sup>-6</sup>	2.9x10 <sup>-5</sup>
150	3,600	2.4x10 <sup>-4</sup>	2.4x10 <sup>-4</sup>	2.4x10 <sup>-4</sup>
200	180	5.6x10 <sup>-3</sup>	5.6x10 <sup>-3</sup>	5.6x10 <sup>-3</sup>

\* From the summaries made by Rothman (60) and Clayton and Fischer (61), the oxidation kinetics at 232 to approximately 400° C is:

$$\text{Pre-Transition } \Delta W^3 = 6.36 \times 10^{11} \exp(-13,636/T) t, \text{ Post-Transition } \Delta W = 75.3 \exp(-556/T) + 1.12 \times 10^5 \exp(-12,529/T) (t-t_t), \text{ and } t_t = 6.73 \times 10^{-7} \exp(11,975/T),$$

where "ΔW" is weight grain (mg/dm<sup>2</sup>), "t" is time (day), and "t<sub>t</sub>" is time to transition (days).

\* Zircaloy density is 6.56 (91) and radiation effects are assumed insignificant after fission products decay.

**Table 3. Rates of Dissolution, and Precipitation and Convection in J-13 Well Water (Eq.[3] and Eq.[4])**

	Dissolution Rate (Flow-through Tests)		Dissolution Rate (Electrochemical Tests)	Rates of Precipitation and Convection (Semi-static Tests)	
	25° C	85° C	25° C	25° C	85° C
U	(0.3 ~ 1.2) x10 <sup>-6</sup> g/day <sup>a</sup> (71)	<sup>b</sup> (92)	(10 <sup>-6</sup> ~ 10 <sup>-3</sup> ) g/day <sup>c</sup> (75,76)	~ 1.5x10 <sup>-6</sup> g/day <sup>d</sup> (15)	~ 8.8x10 <sup>-6</sup> g/day <sup>d</sup> (15)

- <sup>a</sup>: Dissolution rates were normalized over the surface area of 205 cm<sup>2</sup> to compare with those from immersion tests. Dissolution rates for 20 to 250 days are used.
- <sup>b</sup>: Direct measurements were not made at 85° C in J-13 well water containing approximately 2x10<sup>-3</sup> M bicarbonate ions and other constituents. Indirect data were obtained in pure carbonate/bicarbonate solutions. Approximately 3.4 and 21.3 times the dissolution rates increased by raising temperature from 23 to 75° C in 2x10<sup>-2</sup> and 2x10<sup>-4</sup> M carbonate/bicarbonate solutions, respectively, without minor pH corrections.
- <sup>c</sup>: Dissolution rates are from UO<sub>2</sub> tests in chloride solutions. Values vary significantly, depending on corrosion potentials under various oxidizing conditions, including the radiation effects.
- <sup>d</sup>: Cycle 2 tests for 180 days were corrected, based on Tc-99 releases, to exclude any undissolved fuel grains from the stripping process of the altered layer on SF surfaces. Cycle 2 tests were retests of first-cycled samples that had been placed in new leachant, after removing the altered layer.

Figure. Examples of Size and Distribution of Pits

Note: (Pit Diameter versus Time for 18Cr-12Ni-2Mo-Ti Stainless Steel in 0.1N H<sub>2</sub>SO<sub>4</sub> + 0.1N NaCl. Nominal pit size observed is in the range of  $\mu\text{m}$  to mm (93), and pit density is for 304 Stainless Steel after potentiostatic polarization in 1M NaCl solution (94). "d" is pit diameter and "t" is time. (reprinted with permission))

