

Evaluation of Carbon 14 Release from Irradiated Zircaloy Fuel Cladding Through a Long-Term Static Leaching Test

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Abstract

Zircaloy cladding of the spent nuclear fuel, which is highly activated and contaminated, is expected to be disposed of in a deep underground geological repository, both in the once-through and recycling fuel cycles. Carbon 14 (C-14), mainly originated from the nitrogen impurity in Zircaloy cladding and formed through the $^{14}\text{N}(n, p)^{14}\text{C}$ reaction in the reactor, is a typical activation product. In a preliminary performance assessment of the deep geological disposal in Japan, C-14 gave a significant dose impact, which is due to the relatively large inventory, relatively long half-life, i.e., 5730 years, higher release rate and the chemical speciation and consequent migration parameters. In a preliminary Japanese safety case, relatively high IRF (instant release fraction), 20%, was assumed regarding the oxide film formed on the metal surface as a source of the instant release.

With respect to this source term issue, we have prepared an irradiated BWR fuel cladding (Zircaloy-2, average rod burnup of 41.6 GWd/t) which has an external oxide film of 25.3 μm thickness. Although the specific activity in oxide was approximately 3 times higher than the base metal activity, due to the additional C-14 generation by the $^{17}\text{O}(n, \alpha)^{14}\text{C}$ reaction, the C-14 abundance in the oxide was less than 10% of total inventory. A static leaching test using the cladding tube was carried out in an air-tight vessel filled with a deoxygenated dilute NaOH solution (pH of 12.5) at room temperature. After 6.5 years, C-14 was found in each leachate fraction of gas phase and dissolved organics and inorganics, the total of which was less than 0.01% of the entire C-14 inventory of the immersed cladding tube. Both the C-14 abundance and the low leaching rate suggests that C-14 in oxide does not have a significant impact on the IRF in the safety case.

1. Introduction

One of the typical activation products in the radioactive waste from the nuclear fuel cycle is Carbon 14 (C-14) which is mainly generated by a $^{14}\text{N}(n, p)^{14}\text{C}$ reaction in the nuclear reactor. In a preliminary performance assessment of the deep geological disposal in Japan [1], C-14 provided a significant exposure dose due to the large inventory, relatively long half-life, i.e., 5730 years, higher release rate, and the speciation and consequent migration parameters. The oxide film formed on the Zircaloy cladding surface was regarded as a source of instant release while the release of radionuclides from the metal matrix was regarded as the corrosion-related congruent release. The Zircaloy corrosion rate of 0.02 $\mu\text{m}/\text{y}$ and the 20% IRF (instant release ratio) of the spent cladding waste were set as the source term parameters in this preliminary safety case, in which the speciation of C-14 was assumed to be an aqueous organic.

Despite the presence of many studies on this issue, the basic information is still sparse on radionuclide inventory, release behavior of radionuclides and Zircaloy corrosion. For this source term issue, we

have prepared an irradiated BWR fuel cladding (Zircaloy-2, average rod burnup of 41.6 GWd/tU) which has an external oxide film with a thickness of 25.3 μm . The inventory of C-14 was determined by a wet chemical treatment and liquid scintillation counting of C-14 activity using different parts of the cladding such as the base Zircaloy metal, oxide, and metal with and without oxide film. Then in the next step, a static leaching test using cladding tube whose internal oxide was removed was carried out under simulated geological disposal conditions for an exposure period of 6.5 years. This paper describes some details of the experimental work shown in the previous paper [2] on this study.

2. Measurements and tests

(1) Specific radioactivity measurements of C-14

In advance to the leaching test, the specific radioactivity of C-14 was measured as the C-14 inventory in the claddings. The irradiated claddings for this study were obtained from a BWR fuel rod located at the circumference of the fuel assembly. The fuel type is STEP I type, an older fuel type in Japan that uses an 8×8 array in a lattice configuration.

The average burnups are 39.4 GWd/tU for the fuel assembly and 41.6 GWd/tU for the fuel rod, respectively. The irradiation ended in March, 1990. The specimen used in the present work was located between 582 mm and 882 mm from the rod top (Sample ID: F3GT3-H7-481). Table 1 summarizes the characteristics and irradiation conditions of the fuel rod. The claddings had approximately 18 years of cooling-off at the beginning of the leaching test.

Table 1 Characteristics of irradiated cladding.

| | |
|--------------------------------|--------------------------|
| Reactor type | BWR |
| Fuel type | STEP I 8×8 array |
| Material | Zircaloy-2 (Zr liner) |
| Irradiation period | 5 cycles |
| Burnup (Bundle ave., Rod ave.) | 39.4 GWd/tU, 41.6 GWd/tU |
| Cooling-off period | Approximately 18 years |

After the fuel components were removed, the claddings were washed with 6 M of HNO₃ in a warm bath and cut to an appropriate size. The thickness of the external oxide layer was measured, based on optical microscope observations as shown in Fig. 1. The thickness of the cladding specimen was determined by the average value of measurements at 9 points in each of the 8 regions, i.e., at 72 points.

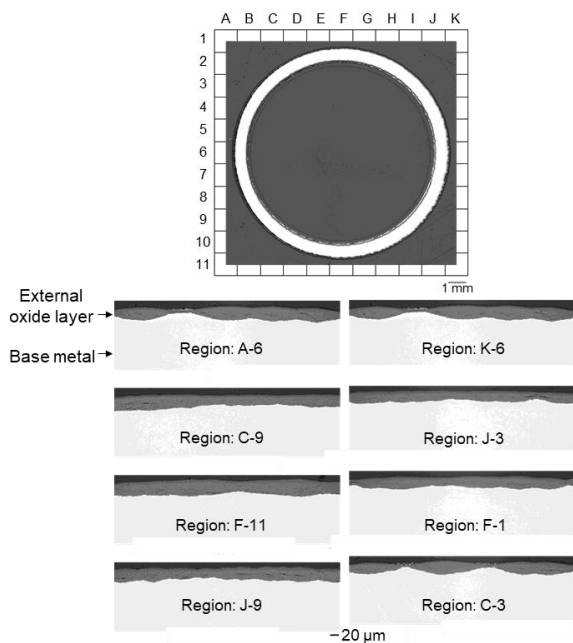


Fig. 1 Measurement of thickness of the external oxide layers.

Four types of samples, i.e., approximately 1 mm thick, ring-shaped claddings and oxide fragment, were obtained for specific activity measurements of C-14, as shown in Fig. 2: (a) the cladding, which has

both internal and external oxide layers; (b) the cladding with the external oxide layer kept after removing the internal oxide by grinding; (c) the Zircaloy base metal without the internal and external oxide layers which were removed by grinding; and (d) the fragment of the external oxide layer. The external oxide layer of Zircaloy was peeled off through vertical pressing of the columnar cladding (approximately 2 cm high) whose interior layer had previously been removed. As a consequence, approximately 0.05 g of oxide was recovered as a powdery fragment.

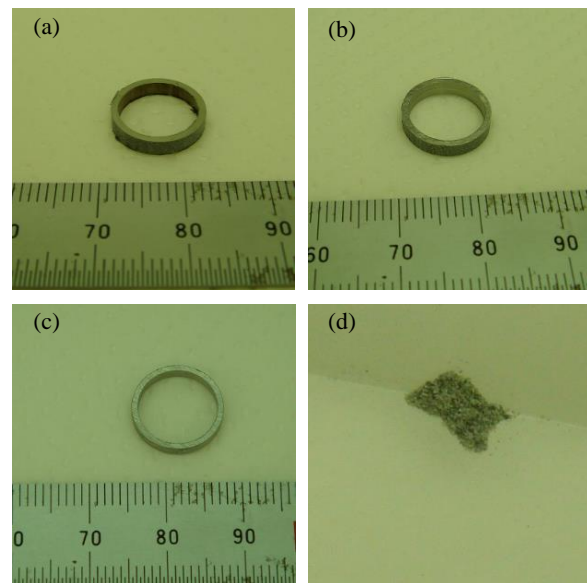


Fig. 2 External appearance of irradiated claddings for C-14 measurement: (a) with internal and external oxide layers in place, (b) with internal oxide removed, (c) with internal and external oxide removed, (d) (external) oxide fragment removed from the cladding.

The C-14 radioactivity in the cladding specimens was measured as shown in Fig. 3. First, the whole body of the cladding or oxide sample was dissolved in an HNO₃ + HF solution and then heated. Carbon components were evaporated by air bubbling for 30 min and oxidized by CuO in CO₂ at 1073 K. The material was then passed through three steps of a dry-ice cold trap to remove tritium and three steps of an alkaline trap (1 M of NaOH) to collect carbon dioxide (¹⁴CO₂). The potential contamination by radioiodine in a volatile state was removed by an AgI precipitation. The C-14 radioactivity in the alkaline traps was measured with a liquid scintillation counter (PerkinElmer Tri-Carb 2900TR).

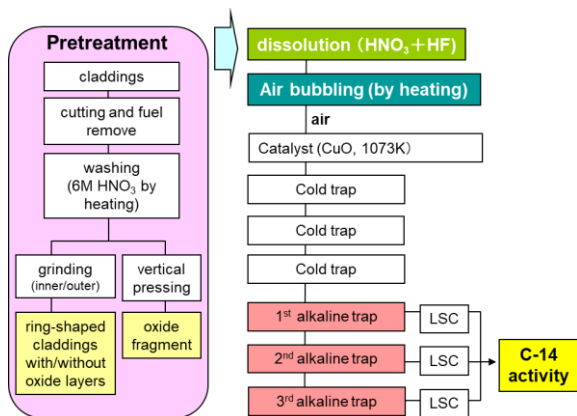


Fig. 3 Measurement procedures of the C-14 specific radioactivity.

(2) Static leaching test

The static leaching test was carried out using the irradiated Zircaloy-2 cladding (F3GT3-H7-481), fore-mentioned, of a 2 cm high cylinder (4.03 g) with an external oxide layer kept, but with its internal oxide layer removed. Final polishing of the cladding interior was done with a 0.02 mm abrasive. A glass vial with a simple cap was filled with 20 ml of diluted NaOH solution adjusted to a pH of 12.5. The solution was deoxygenated before use to achieve an initial ORP (oxidation-reduction potential) of -253 mV. The glass vial was placed on the inside of a stainless steel container and sealed by gasket to maintain the initial inert condition and to prevent leakage of volatile C-14. This immersion procedure was carried out inside a simple glove box with a nitrogen atmosphere. The external view of the test system is shown in Fig. 4.

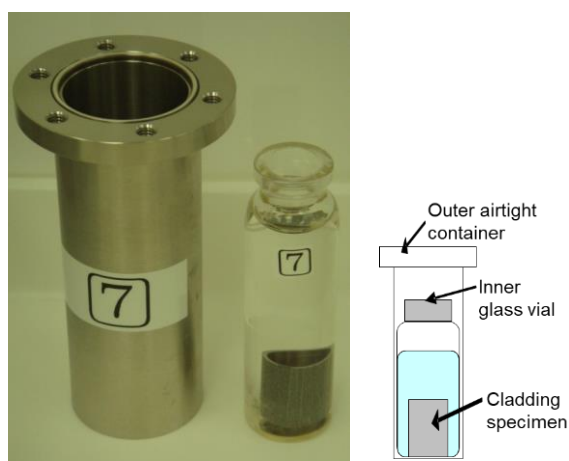


Fig. 4 External view of the test system for the leaching test: the outer stainless steel container (left) and the glass vial in which the cladding is immersed (right) in the photo.

After 6.5 years of immersion and being kept at room temperature of approximately 293 K, the outer and inner containers were opened in a glove bag with a vacuum tube attached. The gaseous C-14 was collected through the tube by using the three steps of an alkaline trap after passing through an oxidation furnace. A portion of the liquid phase was provided for measurement of total dissolved C-14 and dissolved organic and inorganic C-14. The measurement equipment of the dissolved C-14 is shown in Fig. 5. In the total C-14 measurement, an aliquot of leachate was mixed with a carrier carbon (Na_2CO_3 and $\text{C}_2\text{H}_5\text{OH}$), an oxidant (potassium persulfate, $\text{K}_2\text{S}_2\text{O}_8$), a catalyst (AgNO_3), and an acid (H_2SO_4) in a warm vessel. In the organic/inorganic separation method, first the inorganic C-14 was fractionated from another aliquot by bubbling for 30 minutes under acidification. After that, the remaining organics were oxidized with the same reagents used for total C-14 measurement and the volatile C-14 ($^{14}\text{CO}_2$) was collected by an alkaline trap in the same manner as described for total C-14 measurement. Leached C-14 in the alkaline traps was measured by a liquid scintillation counter (PerkinElmer Tri-Carb 3100TR).

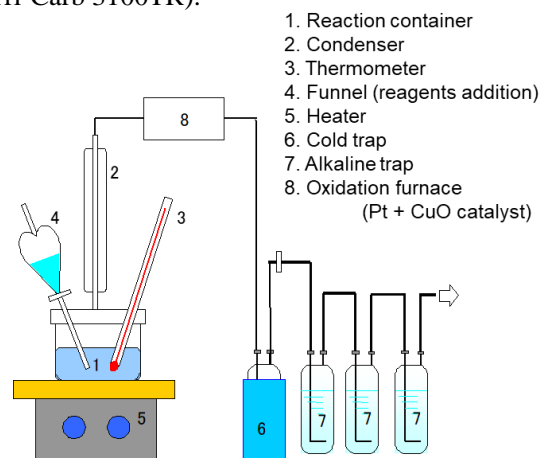


Fig. 5 Measurement equipment of the dissolve C-14.

3. Results and discussions

(1) Distribution of C-14 in irradiated cladding

Table 2 shows the results of C-14 specific activity (Bq/g) measurements for the irradiated cladding samples shown in Fig. 2: (a) the cladding with internal and external oxide, (b) the cladding with external oxide, (c) the cladding base metal, i.e., Zircaloy-2, and (d) the external oxide. The measured activities were normalized to the values at the beginning of the leaching test in Table 2 because the measurement was conducted through two years. For the external oxide, units of grams in the specific activity of oxide are converted into grams of zirconium metal in order to facilitate comparison with the base metal. The average values of (a), (b),

(c) and (d) are 1.49×10^4 , 1.53×10^4 , 1.49×10^4 and 4.04×10^4 Bq/g, respectively.

The radionuclides in cladding oxide are regarded as a source of instant release in the preliminary Japanese safety case, in which 20% of C-14 in cladding was assumed as IRF and the remaining 80% was assumed as the corrosion-related congruent release from the base Zircaloy metal [1]. In Table 2, the specific activity between oxide and base Zircaloy differ by a factor of 3. The C-14 in Zircaloy is mainly generated from the nitrogen impurity as a result of the $^{14}\text{N}(n,p)^{14}\text{C}$ reaction. Given that the nitrogen content in oxide and Zircaloy base metal are equal in amount, the activation calculation using the ORIGEN code suggests that the C-14 content in oxide is larger than the content in base Zircaloy metal due to the additional $^{17}\text{O}(n,\alpha)^{14}\text{C}$ reaction [3]. Based on the cladding geometry (thickness of the base metal and oxide layer in Table 2) and the

density of Zircaloy and the oxide layer, the abundance of C-14 in the oxide and the base Zircaloy can be estimated as 7.5% and 92.5%, respectively, where the oxide density is assumed to be 5.24 g/cm^3 which corresponds to 90% of the theoretical density of zirconia, ZrO_2 (5.82 g/cm^3) [4]. This C-14 distribution corresponds roughly to the C-14 inventory in waste claddings estimated by the fore-mentioned ORIGEN calculation, in which the respective percentages of 3.5% and 96.5% were suggested for the BWR STEP I cladding [3]. It can therefore be concluded from the results of these measurements and calculations that the assumption of 20% IRF in the safety case was somewhat over-conservative. However, the C-14 distribution in oxide for the PWR cladding was measured as 17% [5], which can be attributed to the oxide thickness of the claddings and that the oxide layer of PWR cladding in the literature is especially thick at $80 \mu\text{m}$.

Table 2 Specific activity of C-14 for irradiated claddings and oxide.

| Sample ID | Thickness (μm) | | Specific activity (Bq/g) | | | |
|--------------|-----------------------------|----------------------|---|----------------------------------|-------------------------|---------------------|
| | Base metal | External oxide layer | (a) Cladding with internal and external oxide | (b) Cladding with external oxide | (c) Cladding base metal | (d) External oxide* |
| | | 25.3 | 1.54×10^4 | 1.53×10^4 | 1.49×10^4 | 4.25×10^4 |
| F3GT3-H7-481 | 704.7 | | 1.49×10^4 | | 1.50×10^4 | 3.83×10^4 |
| | | | 1.43×10^4 | | 1.47×10^4 | |

* Units of grams in the oxide are converted to grams of zirconium, not grams of ZrO_2 .

(2) Released C-14 from irradiated cladding after 6.5 years aqueous immersion

Table 3 shows the leached amount of C-14 for the respective fractions measured after 6.5 years of aqueous immersion of irradiated cladding. The gaseous released C-14 (0.317 Bq) is less than the dissolved C-14 species (2.00 Bq in total fraction). The sum of the dissolved inorganic and organic C-14 is 1.64 Bq, which corresponds roughly to the total dissolved C-14. The leached organic C-14 is approximately 3 times of the amount of the inorganic C-14. On the other hand, the speciation of released C-14 was all dissolved organics, reported by previous short-term leaching tests using irradiated PWR cladding [5]. The reason for the discrepancy is not clear, but it could be a difference in the analysis in that the previous conclusion was based on the simple anion exchange property of dissolved C-14. The leaching ratio, which represents the leached amount

(gaseous + dissolved) divided by the initial inventory, is very small at 3.8×10^{-5} or less, i.e. less than 0.01%. Past short-term leaching tests which involve PWRs [5], fore-mentioned, or BWR STEP III [6] cladding also showed small C-14 leaching ratios of less than 4×10^{-5} .

The oxide layer might be a dominant source of C-14 release from irradiated cladding, taking into account the limited C-14 release from the base metal due to the low corrosion rate of Zircaloy [2]. However, regarding the C-14 in oxide as a source of instant release would be too conservative because the released C-14 is less than 3.8×10^{-5} of the total after 6.5 years of immersion. Together with the corrosion behavior of Zircaloy, understanding the mechanism of how the C-14 is released from oxide layer, for example, the solubility of zirconia under deep disposal conditions is a challenge that needs to be addressed.

Table 3 Released C-14 in different fractions measured after 6.5 years aqueous immersion, in Bq.

| Initial inventory | Gas phase | Total dissolved | Dissolved inorganic | Dissolved organic |
|--------------------|-----------|-----------------|---------------------|-------------------|
| 6.17×10^4 | 0.317 | 2.00 | 0.403 | 1.24 |

4. Conclusion

The specific activity of C-14 in the irradiated BWR fuel cladding was measured and found to be 1.49×10^4 Bq/g in the base Zircaloy. The specific activity in the external oxide that might be activated from nitrogen impurity and oxygen was approximately 3 times higher than that in base Zircaloy, which leads to the C-14 distribution of 7.5% to the oxide layer and 92.5% to the base Zircaloy in the cladding. From the 6.5 years of aqueous immersion, the leached C-14 from the irradiated cladding with the adhering external oxide layer was found in gaseous form, as dissolved inorganics and as dissolved organics, whose composition ratios are 16%, 21%, and 63%, respectively. The total C-14 released was less than 0.01% of the C-14 inventory of the cladding. Both the low amount of C-14 in oxide and the low leaching rate indicate that the C-14 in oxide does not have a major impact on the instant release fraction in the safety case. To improve the understanding of these phenomena, knowledge of the radionuclide leaching behavior from the oxide layer is needed. Specifically, the estimation of the gradual release rate from the cladding oxide can be facilitated from the solubility of zirconia under the deep repository ground water conditions. Another future challenge is to clarify the assumed congruence behavior between the corrosion and radionuclide release.

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References

- [1] Federation of Electric Power Companies (FEPC) and Japan Atomic Energy Agency (JAEA). Second progress report on research and development for TRU waste disposal in Japan, 2007.
- [2] Sakuragi, T., Yamashita, Y., Akagi, M., Takahashi, R., Carbon 14 Distribution in irradiated BWR fuel cladding and released Carbon 14 after aqueous immersion of 6.5 years, *Procedia Chemistry*, Volume 21, 2016.
- [3] Sakuragi, T., Tanabe, H., Hirose, E., Sakashita, A., Nishimura, T., Estimation of Carbon 14 inventory in hull and end-piece wastes from Japanese commercial reprocessing operation, *Proc. of the 15th International Conference on Environmental Remediation and Radioactive Waste Management, ICEM2013*, 2013.
- [4] Garzarolli, F., Jung, W., Schoenfeld, H., Garde, A. M., Parry, G. W., Smerd, P. G., Waterside corrosion of Zircaloy fuel rods. EPRI NP-2789, 1982.
- [5] Yamaguchi, T., Tanuma, S., Yasutomi, I., Nakayama, T., Tanabe, H., Katsurai, K., Kawamura, W., Maeda, K., A study on chemical forms and migration behavior of radionuclides in hull waste, *Proc. of the 7th International Conference on Environmental Remediation and Radioactive Waste Management, ICEM1999*, 1999.
- [6] Yamashita, Y., Tanabe, H., Sakuragi, T., Takahashi, R., Sasoh, M., C-14 release behavior and chemical species from irradiated hull waste under geological disposal conditions, *Mater. Res. Soc. Symp. Proc.* 1665, 2014.