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Instant release fractions for ^{14}C, ^{60}Co, and ^{125}Sb from irradiated Zircaloy oxide film

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Abstract

The oxide films formed on spent fuel claddings are regarded as a potential source of the instantaneous release of radionuclides, such as ^{14}C, after waste disposal. We investigated the instant release fraction using the irradiated oxide exfoliated from a Zircaloy-2 water rod, whose bundle burnup was 53.0 GWd/MTU. We performed a rapid leaching test in a dilute NaOH solution (pH of 12.5) for 10 min in an ultrasonic bath to ensure the release of radionuclides. The activity ratios of the leached amount to the total amount for ^{14}C, ^{60}Co, and ^{125}Sb were extremely low at approximately 10^{-4} to 10^{-3}, among which the maximum value was 2.65×10^{-3} for ^{125}Sb. These ratios were higher than that predicted from the thermodynamic solubility of ZrO_2, i.e., less than 10^{-6}. However, given the low ratios, it is too conservative to regard the inventory of all radionuclides in the Zircaloy oxide as instantaneous release. A small part of the released ^{14}C was found as volatile species.

INTRODUCTION

Spent fuel cladding is highly activated and strongly contaminated, and it is disposed of in underground repositories. A typical activation product in activated metal waste is ^{14}C, which is mainly generated by the $^{14}N(n,p)^{14}C$ reaction and potentially produces a significant exposure dose owing to large inventory, long half-life (5730 years), rapid release rate, and the mobile speciation in repository environments. In the preliminary safety case in Japan, the release of radionuclides from a metal matrix (bulk Zircaloy) is 80% of cladding inventory and is regarded as corrosion-related congruent release. Whereas cladding oxide films having 20% inventory are regarded as a source of the instant release fraction (IRF) [1,2]. In the 1990s, researchers conducting a study using spent pressurized water reactor (PWR) cladding with an 80 µm thick oxide film found that the oxide inventory of ^{14}C contains 17% of the remaining radionuclides which they suggested was constitutive of the IRF [3]. Guenther et al. [4] estimated 15% oxide inventory for US cladding with a 50 µm oxide film.

In contrast, recently, the IRFs for the ^{14}C inventory of oxide films have been reported as approximately 9% for Japanese PWRs and 0.8% for boiling water reactors (BWRs) based on the ORIGEN calculation performed using the oxide thickness data of Japanese claddings for different types of fuels with varying burnup [5]. Another study has found a negligible IRF through the long-term aqueous immersion test of an irradiated cladding with an adhering external oxide film [6]. However, the direct evidence of the release of radionuclides from Zircaloy oxide under repository environment conditions has not been reported until now.

In this study, we have prepared Zircaloy oxide using a water rod as an analog of cladding. The water rod is one of the structural components of BWR fuel and is fabricated from Zircaloy-2. Therefore, it is also a part of the waste. The water rod is thicker than the cladding and is located at the center of the fuel assembly. It is exposed to the same water corrosion environment as the cladding during reactor operation. Unlike the cladding, the water rod is not contaminated by fuel components. This is an advantage when investigating activation products such as ^{14}C and the internal and external oxide films obtained from the water rod can be used for experiments. The specific activity of the radionuclides from the base metal and oxide parts of the water rod were obtained because relatively little is known about the radionuclide inventory in irradiated Zircaloys. Rapid leaching tests were carried out in a dilute NaOH solution with a pH of 12.5, which parallels the pH levels of cementitious repository conditions. To ensure the release of radionuclides as an equivalence to the IRF, a batch type immersion system was mildly accelerated by ultrasound. Leached radionuclides and the solubility of ZrO_2 are discussed.

MATERIALS AND METHOD

Specimen

A spent water rod was obtained from the spent BWR fuel assembly, which is the STEP III type fuel with the lattice configuration of a 9 × 9 array irradiated in the Fukushima Daini nuclear power plant, Japan (Bundle ID: 2F1Z3). The average burnup for the assembly was 53.0 GWd/MTU. The specimen cut from the water rod was located between 1180 mm and 2370 mm from the top. Table 1 summarizes the characteristics and irradiation conditions of the water rod [7].

The water rod was cut to a height of 20 mm and washed with 3 M HNO_3 in a warm bath. The thicknesses of the internal and external oxide films were found to be 11.0 and 9.0 µm, respectively. A subsample coupon of the water rod base metal was obtained for measuring the specific activity of radionuclides by grinding the internal and external oxide films. The surface oxide film of Zircaloy was peeled off in two steps by bending the water rod coupon in the vertical and horizontal directions using a press machine. As a consequence, 369 mg of oxide, which included the internal and external oxide films, was recovered as a powdery fragment by repeating the bending process for several coupons, which were equivalent to a total water rod length of 160 mm. The appearances of the water rod specimen and oxide are shown in Figure 1. The coupon broke into two in the second bending process due to embrittlement, as shown in Figure 1(b).

Table I. Irradiation conditions and characteristics of water rod [7].

Reactor and fuel type	BWR, STEP III 9 × 9 array A type
Bundle ID	2F1Z2
Material	Zircaloy-2
Ring diameter	24.9 mm
Irradiation period	5 cycles, 1957 days (July 1996–January 2003)
Burnup (Bundle average)	53.0 GWd/tU

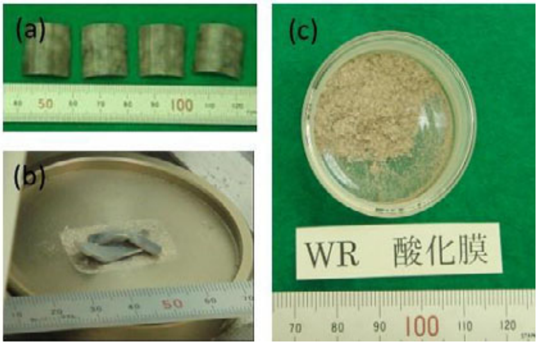

Figure 1. Specimen images: (a) Irradiated water rod cut to a height of 2 cm and divided into six parts, (b) Pressed, bended and broken water rod for peeling off the oxide film, (c) Powdery oxide fragments removed from the water rod.

Procedure for radioactive measurement and accelerated leaching test

The ^{14}C radioactivity and other gamma emitting nuclides in the water rod samples were measured using the same method as that employed for the previous measurement of the cladding samples [6,8]. The samples were dissolved in an HNO_3 + HF solution and then heated. The gamma radionuclides in the dissolved solution were measured. The carbon components in the dissolved solution were evaporated by air bubbling for 30 min and oxidized by CuO in CO_2 at 1073 K. Then, the material was 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 ($^{14}CO_2$). The potential contamination by radioiodine in a volatile state was removed through AgI precipitation. The ^{14}C radioactivity in the alkaline traps was measured by utilizing a liquid scintillation counter (PerkinElmer Tri-Carb 2900TR).

A semi-accelerated leaching test was carried out under ultrasound using the irradiated Zircaloy-2 oxide obtained from the water rod. An oxide sample of approximately 0.1 g was immersed in a flask filled with 10 mL of a dilute NaOH solution with a pH of 12.5. Then, the flask was set into an ultrasound bath, which had an oscillation frequency of 40 kHz, for 10 min at room temperature in air atmosphere. During the immersion with ultrasound, volatilized ^{14}C was collected using the alkaline traps after the oxidized by CuO at 1073 K. After 10 min, the liquid and solid phases were separated through 0.22 μm filtration. The radionuclides in the alkaline traps and leachates were measured. The inorganic ^{14}C in the leachates was fractionated with an added carrier carbon (Na_2CO_3) by bubbling for 30 min under acidification. Then, the remaining organic carbon species were oxidized and volatile ^{14}C was collected in the same manner as described above. This immersion test was repeated three times (Samples 1 to 3).

RESULTS AND DISCUSSION

Radionuclides concentration in water rod

Table II shows the specific activity (Bq/g) of ^{14}C, ^{60}Co, and ^{125}Sb for the irradiated water rod base metal and oxide. Note that the units of grams in the specific activity of the oxide are converted into grams of zirconium metal to facilitate comparison with the base metal. The ^{60}Co activity of the oxide is considerably higher than that of the base metal. This may be due to the contamination of the water rod surface by corrosion products in cooling water. In Figure 2, the present result of the ^{14}C activity of the base metal is compared with those of the spent fuel claddings obtained from various reactors in different countries. The activity appears to increase with burnup. The ^{14}C activity of the water rod is comparable with those of the claddings.

Table II. Specific activity of radionuclides for water rod samples. The activity values of ^{60}C and ^{125}Sb, which are short half-life nuclides, are corrected at the time when irradiation is stopped (January 2003).

	^{14}C	^{60}Co	^{125}Sb
Base metal	4.69×10^4 Bq/g	7.63×10^6 Bq/g	1.46×10^8 Bq/g
Oxide film*	4.18×10^4 Bq/g	6.36×10^8 Bq/g	7.53×10^7 Bq/g

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

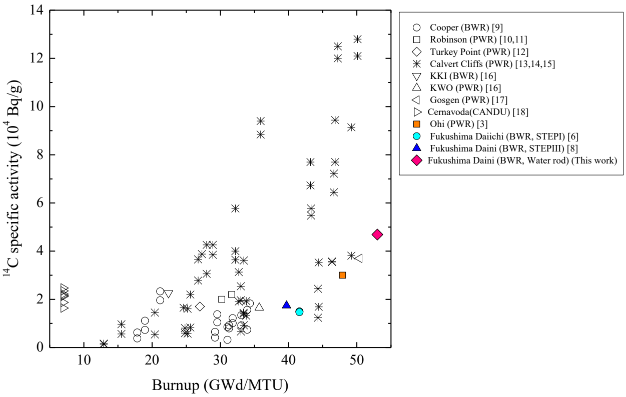

Figure 2. Specific activity of ^{14}C for claddings and water rod as a function of the burnup obtained from different reactors.

In the present work, the ^{14}C activity of the oxide and base metal is comparable, whereas the previous results for claddings suggest that the specific activity of the oxide is higher than that of the base Zircaloy [3,6]. For the BWR cladding (STEP I type, 8 × 8 array), the difference was a factor of 2.8 [6]. This discrepancy is not fully understood at present. However, it may be partly explained by the difference in irradiation conditions for the neutron spectrum, as discussed below.

This hypothesis was examined through simple calculations in the following manner: The neutron spectrum was analyzed using the three-dimensional Monte Carlo transport calculation code (MCNP). The axial direction of the fuel region was divided into 24 nodes, where the neutrons were classified into fast, epithermal, and thermal neutrons. The void ratio and node average enrichment were evaluated based on actual operation data. The cladding and water rod were assumed to be arranged in the same assembly close to the circumference and center, respectively. Table III summarizes the percentages of neutron flux for three energy groups corresponding to fast, epithermal, and thermal neutrons. The neutron spectrum for the water rod shifted to a lower energy level than that for the cladding. More specifically, the thermal neutron flux for the water rod is 1.5 times that for the cladding. Unlike the cladding, the inside of the hollow water rod is also surrounded by water, which acts as a neutron moderator. The thermal cross section is relatively larger for the $^{14}N(n,p)^{14}C$ reaction, whereas the epithermal cross section is larger for the $^{17}O(n,\alpha)^{14}C$ reaction. As the $^{14}N(n,p)^{14}C$ reaction is more prominent in the base Zircaloy compared to the oxide, the ^{14}C concentration in the base Zircaloy water rod is higher compared to the cladding. This might be the reason for the comparable ^{14}C concentration between the water rod oxide and base metal.

Table III. Percentages of neutron flux for three energy ranges calculated by MCNP at the locations of cladding and water rod.

	Thermal neutron (~ 6.25×10^{-7} MeV)	Epithermal neutron (6.25×10^{-7}–5.55×10^{-3} MeV)	Fast neutron (5.55×10^{-3}–2.00×10^{1} MeV)
Water rod	15.1%	26.8%	58.1%
Cladding	10.4%	26.7%	62.9%

Released radionuclides from Zircaloy-2 oxide

Table IV shows the leached ratios obtained in the semi-accelerated leaching tests. The leached ratio represents the leached amount (Bq) divided by the initial inventory in the oxide sample. The gaseous, dissolved organic, and dissolved inorganic fractions are obtained for ^{14}C. Most of the released ^{14}C is present in the dissolved inorganic fraction. A small amount of gaseous ^{14}C is released only in the third test. The total leached ratio of ^{14}C is less than 2×10^{-3}. The leached ratios for ^{60}C and ^{125}Sb are approximately 10^{-4} and 10^{-3}, respectively. All values are sufficiently small. The largest leached ratio is 2.65×10^{-3}, which is obtained for ^{125}Sb.

In the previous static leaching tests performed using irradiated BWR cladding with an attached oxide film, the leached ratio of ^{14}C was less than 10^{-4} after 6.5 years [6]. A similar result obtained using CANDU cladding with an oxide film showed that the leached ratio of ^{14}C was 7.7×10^{-4} after 18 months [18]. Along with the aforementioned data, the present result reveals that the IRF of irradiated Zircaloy is negligible compared with the 20% IRF assumed in the Japanese safety case [1,2].

The radionuclide release from Zircaloy oxide might be a potential congruent release with the dissolution of zirconia (ZrO_2). The solubility of zirconia has been studied for numerous years because the zirconium isotope (^{93}Zr) is regarded as a key nuclide for high-level radioactive waste disposal [19-22]. In the thermodynamic database, the solubility product of ZrO_2 is $\log K_{sp} = -63.0 \pm 1.6$ [20]. Using this thermodynamic data in the Zr–OH system, the amount of Zr species in the aqueous phase has been calculated using the equation given below without any corrections of the activity coefficient for simplicity.

$$Zr^{4+} + nH_2O = Zr(OH)_n^{4-n} + nH^+$$

where n = 0–6. The hydrolysis constants ($\log \beta_{1,n}$) corresponding to n = 0–4 and n = 5, 6 were obtained from the studies by Brown et al. [20] and Rai et al. [22], respectively. The solubility product value by Rai et al. ($\log K_{sp} = -56.19$) [22] was used for calculating n = 5 and 6 species.

The sum of the concentrations for Zr species in equilibrium with ZrO_2 at a pH of 12.5 is 4.96×10^{-8} mol/L, which can be corresponding to a dissolved ratio of 6.16×10^{-7} under the solid to liquid ratio in this study (0.1 g ZrO_2/10 mL solution). The leached ratios of radionuclides obtained in the present study are larger than the above predicted dissolved ratio. This discrepancy might be attributed to the underestimation of ZrO_2 solubility where the presence of polynuclear, carbonate, and colloidal species passed through the 0.22 μm filter are not taken into account. On the contrary, the ultrasound might be extremely caustic, so that excess Zr and radionuclides are discharged. The overestimation due to contamination of the oxide film is also possible. As mentioned earlier, the specific activity of ^{60}C, which was two orders of magnitude higher for the oxide compared to the base metal (Table II), suggests contamination. Even though the details of the mechanism of radionuclide release from the irradiated oxide should be investigated further, it is too conservative to regard the ^{14}C and other activation products in the oxide as the IRF because the leached ratio is negligible and ZrO_2 is poorly soluble under the conditions of waste disposal.

Table IV. Leached ratio of radionuclides to total activity from water rod oxide obtained in the semi-accelerated leaching test.

	Gaseous ^{14}C	Dissolved inorganic ^{14}C	Dissolved organic ^{14}C	^{60}C (dissolved)	^{125}Sb (dissolved)
Sample 1	ND	1.52×10^{-3}	ND	9.58×10^{-4}	2.65×10^{-3}
Sample 2	ND	1.36×10^{-3}	ND	3.50×10^{-4}	1.29×10^{-3}
Sample 3	8.14×10^{-4}	1.18×10^{-3}	ND	3.62×10^{-4}	1.29×10^{-3}

ND represents under the detection limit.

CONCLUSIONS

The instant release behavior of ^{14}C and other activation products of ^{60}Co and ^{125}Sb obtained from irradiated Zircaloy-2 oxide exfoliated from a water rod was investigated. In the inventory analysis performed prior to the leaching test, the values of radionuclide activity in the water rod base metal and oxide were obtained and found to be comparable to those for irradiated claddings. Rapid leaching tests semi-accelerated by ultrasound were performed using the exfoliated oxide, and results showed a negligible IRF, leached ratios of approximately 10^{-4} to 10^{-3}, and a maximum leached ratio of 2.65×10^{-3} for ^{125}Sb. Even though the immersion period was short, it can be concluded that the assumption of 20% IRF in the safety case was too conservative. However, the congruent leaching of radionuclides along with the dissolution of oxides has not yet been explained in detail based on the thermodynamic calculation of ZrO_2 solubility. This congruent release should be further examined. In addition, the characteristics of the irradiated Zircaloy oxide related to the different behavior for each nuclide should be investigated for improving the understanding of disposal safety.

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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. The Nuclear Waste Management Organization of Japan (NUMO), NUMO Safety Case, NUMO-TR-18-03 (2018). (in Japanese)
3. T. Yamaguchi, S. Tanuma, I. Yasutomi, T. Nakayama, H. Tanabe, K. Katsurai, W. Kawamura, and K. Maeda, Proc. ASME 7th International Conference on Environmental Remediation and Radioactive Waste Management, Sep. 26-30, Nagoya, Japan (1999).
4. R. J. Guenther, D. E. Blahnik, L. E. Thomas, D. L. Baldwin, and J. E. Mendel, Proc. Spectrum 90 Conference, Sept. 30-Oct. 3, Knoxville, TN (1990).
5. T. Sakuragi, H. Tanabe, E. Hirose, A. Sakashita and T. Nishimura, Proc. ASME 15th International Conference on Environmental Remediation and Radioactive Waste Management, Sep. 8-12, Brussels, Belgium (2013).
6. T. Sakuragi, Y. Yamashita, M. Akagi and R. Takahashi, Procedia Chem **21**, 341-348 (2016).
7. Japan Nuclear Energy Safety Organization (JNES), Verification Program of BWR 9×9 Fuel (2007) (in Japanese).
8. Y. Yamashita, H. Tanabe, T. Sakuragi, R. Takahashi, and M. Sasoh, Mater Res Soc Symp Proc **1665**, 187-194 (2014).
9. R. J. Guenther, D. E. Blahnik, T. K. Campbell, U. P. Jenquin, J. E. Mendel, L. E. Thomas, and C. K. Thornhill, ATM-105. PNL-5109-105, Pacific Northwest Laboratory, Richland, WA (1991).
10. J. O. Barner, ATM-101. PNL-5109 Rev.1, Pacific Northwest Laboratories, Richland, WA (1985).
11. C. N. Wilson, HEDL-TME 85-22, Westinghouse Hanford Company, Richland, WA (1987).
12. R. A. Van Konynenburg, C. F. Smith, H. W. Culham, and H. D. Smith, Mater Res Soc Symp Proc **84**, 185-196 (1987).
13. R. J. Guenther, D. E. Blahnik, T. K. Campbell, U. P. Jenquin, J. E. Mendel, L. E. Thomas, and C. K. Thornhill, ATM-103. PNL-5109-103, Pacific Northwest Laboratory, Richland, WA (1988).
14. R. J. Guenther, D. E. Blahnik, U. P. Jenquin, J. E. Mendel, L. E. Thomas, and C. K. Thornhill, ATM-104. PNL-5109-104, Pacific Northwest Laboratory, Richland, WA (1991).
15. R. J. Guenther, D. E. Blahnik, T. K. Campbell, U. P. Jenquin, J. E. Mendel, and C. K. Thornhill, ATM-106. PNL-5109-106, Pacific Northwest Laboratory, Richland, WA (1988).
16. A. Bleier, K. H. Neeb, R. Kroebel, and H. W. Wiese, Proc. International Conference on Nuclear Fuel Reprocessing and Waste Management, Aug. 23-27, Paris, France (1987).
17. M. Herm, R. Dagan, E. González-Robles, N. Müller, and V. Metz, MRS Adv **3**, 1031-1037 (2018).
18. C. Bucur, M. Fulger, I. Florea, and A. Tudose, Radiocarbon **60**, 1773-1786 (2018).
19. C. Ekberg, G. Kallvenius, Y. Albinsson, and P. L. Brown, J Solution Chem **33**, 47-79 (2004).

20. P. L. Brown, E. Curti, B. Grambow, and C. Ekberg, “Chemical Thermodynamics of Zirconium”, Chemical Thermodynamics vol.8, ed. F. J. Mompean et al. (Elsevier, 2005).
21. T. Kobayashi, T. Sasaki, I. Takagi, and H. Moriyama, J Nucl Sci Technol **44**, 90 (2007).
22. D. Rai, A. Kitamura, M. Altmaier, K. M. Rosso, T. Sasaki, and T. Kobayashi, J Solution Chem **47**, 855-891 (2018).