Determination of Uranium, Plutonium, Cesium and Europium Isotopes in Nuclear Fuel Claddings by Isotope Dilution Mass Spectrometry and γ -Ray Spectrometry†

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Isotope dilution mass spectrometric (IDMS) and γ -ray spectrometric (GRS) methods have been used for the determination of uranium, plutonium, cesium and europium isotopes in cladding from pressurized water reactor nuclear fuel irradiated in a power reactor. A dissolution of cladding samples was performed through a two-step procedure, washing with 8 M HNO_3 at 90 °C and dissolving with 2 M HF at 25 °C followed by dissolving with aqua regia at 90 °C. After the dissolution procedure, the chemical composition of insoluble residue (< 2 wt. %) was identified using a γ -ray spectrometry. The isotopic compositions and their contents of uranium and plutonium and the activities of cesium and europium isotopes found in the dissolving and washing solutions of the cladding specimen from high burnup nuclear fuel, were compared with those found in a dissolving and washing solutions of the cladding specimen from low burnup nuclear fuel.

Keywords: Isotope dilution mass spectrometry, γ -Ray spectrometry, Fuel cladding, Uranium, Plutonium, Cesium, Europium.

INTRODUCTION

Pressurized water reactor (PWR) cladding is made of zirconium alloy (zircaloy) and there are three main types of activities associated with it *i.e.*, activation products, fission products and actinides. The amounts of activation products depend on the irradiation conditions and the neutron flux. The amounts of fission products and actinides depend on the quantity of spent fuel remaining in the cladding after de-cladding. Some fission products will be driven into the cladding by fission recoil and there is also likely to be a penetration of the cladding as a result of diffusion along grain boundaries. α -Spectra of the cladding surfaces were obtained for pressurized water reactor cladding samples and the results have shown very little penetration of the zircaloy surface by α -emitters¹. A quantitative evaluation of radionuclides in spent fuel cladding is of great importance with respect to the final waste disposal and environmental aspects and the recycling of the cladding. In the decontamination practice to reduce the hazards arising from the radioactivity in spent fuel claddings, the distribution of actinides in the fuel cladding is of particular importance^{1,2}.

In this work, washing and dissolving experiments have been performed to evaluate the distribution of U, Pu, Cs and Eu isotopes on the surface and the interior of spent nuclear

fuel cladding specimens. The isotopic compositions and their contents of U and Pu and the activities of Cs and Eu isotopes (γ -emitters) in the washed solutions as well as the dissolved solutions were determined using isotope dilution mass spectrometric (IDMS) and γ -ray spectrometric (GRS) methods, respectively.

EXPERIMENTAL

Certified ^{233}U (99.470 atom %) spike was obtained from Oak Ridge National Laboratory (ORNL). This spike solution was prepared by dissolving their oxides in 8 M HNO_3 -0.01 M HF. NBL CRM 129 U_3O_8 powder (New Brunswick Laboratory) and a U standard solution (Spex Industries Inc.) were used as a standard reference material for the U. A certified ^{242}Pu spike solution (99.9033 atom %, IRMM-044) was obtained from the Institute for Reference Materials and Measurements³. Two kinds of cladding specimens, H-1 (low burnup fuel cladding) and H-2 (high burnup fuel cladding) were prepared from the spent nuclear fuel rods of a PWR type. S-1, S-2 and S-3 cladding wastes, which were previously decontaminated by refluxing with nitric acid, were prepared for the dissolution experiments. The isotopic compositions of U and Pu in the unspiked and spiked samples were determined using a thermal

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TABLE-2
DISTRIBUTION OF γ -EMITTERS IN CLADDING SAMPLES

Nuclide	Activity (Bq/g-sample)			
	H-1(W)	H-2(W)	H-1(D)	H-2(D)
^{134}Cs	$6.46 \times 10^4 \pm 1.92 \times 10^3$	$4.63 \times 10^6 \pm 1.68 \times 10^4$	$3.06 \times 10^4 \pm 1.16 \times 10^3$	$1.55 \times 10^6 \pm 8.18 \times 10^3$
^{60}Co	$< 1.23 \times 10^3$	$2.63 \times 10^5 \pm 4.91 \times 10^3$	$1.63 \times 10^5 \pm 1.84 \times 10^3$	$3.26 \times 10^5 \pm 5.47 \times 10^3$
^{137}Cs	$9.10 \times 10^6 \pm 1.94 \times 10^4$	$1.04 \times 10^8 \pm 9.03 \times 10^4$	$1.12 \times 10^7 \pm 1.98 \times 10^4$	$3.40 \times 10^7 \pm 3.83 \times 10^4$
^{154}Eu	$1.88 \times 10^5 \pm 5.84 \times 10^3$	$3.91 \times 10^6 \pm 4.45 \times 10^4$	$2.12 \times 10^5 \pm 6.29 \times 10^3$	$1.25 \times 10^6 \pm 1.70 \times 10^4$
^{155}Eu	$3.67 \times 10^4 \pm 3.49 \times 10^3$	$1.12 \times 10^6 \pm 1.46 \times 10^4$	$3.45 \times 10^4 \pm 3.48 \times 10^3$	$3.40 \times 10^5 \pm 8.96 \times 10^3$
^{125}Sb	$< 1.81 \times 10^4$	$4.39 \times 10^6 \pm 1.18 \times 10^5$	$8.87 \times 10^5 \pm 1.32 \times 10^4$	$4.74 \times 10^6 \pm 3.64 \times 10^4$
^{95}Zr	$1.99 \times 10^4 \pm 3.91 \times 10^3$	$3.08 \times 10^5 \pm 1.01 \times 10^4$	$2.07 \times 10^4 \pm 4.55 \times 10^3$	$1.08 \times 10^5 \pm 1.06 \times 10^4$

H-1, low burnup cladding; H-2, high burnup cladding; W, washed solution; D, dissolved solution.

fuel burnup¹. On the other hand, the activities of γ -emitters found in the washed and dissolved solutions of the same cladding, *i.e.*, H-1(W) and H-1(D) and H-2(W) and H-2(D) are similar on the whole, except ^{60}Co and ^{125}Sb . These results indicate that the γ -emitters including Cs and Eu isotopes were distributed similarly on the surface and in the interior of fuel cladding, regardless of fuel burnup.

Isotopic compositions of U, Pu, Cs and Eu in fuel cladding: Tables 3 and 4 show the isotopic compositions in atom % of U and Pu in the washed and dissolved solutions of H-1 and H-2 claddings measured by TIMS, respectively. Contributions of various isobars to the U and Pu fractions were identified by monitoring the mass peaks from 233-244. Data in the tables show that there is no isobaric effects from other elements. These data for H-1 and H-2 claddings are similar to those obtained from the high and low burnup spent fuels of a pressurized water reactor type⁶. As a result, we found that satisfactory chromatographic separation of U and Pu in the cladding samples, could be achieved by the procedures in Fig. 2. Table-5 shows a comparison of the isotopic ratios for U, Pu, Cs and Eu in the washed and dissolved solutions of H-1 and H-2

claddings. As can be seen in the tables, all of the isotopic ratios for U, Pu, Cs and Eu in H-2(W) and H-2(D), are similar to each other. On the other hand, in the case of those in H-1(W) and H-1(D), there is a distinct difference between the two values. It may be inferred that the actinides and fission products were occluded into the surface oxide layer formed on the surface of the cladding through the repetition of the adsorption and adhesion of fuel and oxidation of the surface during irradiation¹. Therefore, it can be concluded that the difference between the isotopic ratios in the washed solution to that in the dissolved solution decreases with the progression of the fuel burnup.

Quantities of U and Pu isotopes in fuel cladding: Tables 6 and 7 show the quantities of U, Pu and their isotopes in the washed and dissolved solutions of H-1 and H-2 claddings as determined by IDMS. As shown in the tables, the quantities of U and Pu determined in the washed solution samples are much more than those of the dissolved solutions and the quantities of U and Pu found in H-2(W) are higher than those found in H-1(W). This means that the U and Pu in the claddings are mainly present on the surface and only a small amount is

TABLE-3
ISOTOPIC COMPOSITIONS OF U SEPARATED FROM CLADDING SAMPLES

Sample	Atom (%)			
	^{234}U	^{235}U	^{236}U	^{238}U
H-1(W)	0.025 ± 0.003	0.960 ± 0.003	0.510 ± 0.004	98.501 ± 0.006
H-1(D)	0.028 ± 0.006	0.774 ± 0.008	0.583 ± 0.010	98.596 ± 0.059
H-2(W)	0.026 ± 0.002	0.675 ± 0.006	0.685 ± 0.006	98.613 ± 0.014
H-2(D)	0.026 ± 0.008	0.699 ± 0.007	0.673 ± 0.006	98.596 ± 0.019

TABLE-4
ISOTOPIC COMPOSITIONS OF Pu SEPARATED FROM CLADDING SAMPLES

Sample	Atom (%)				
	^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu	^{242}Pu
H-1(W)	1.242 ± 0.012	62.127 ± 0.040	22.991 ± 0.031	6.663 ± 0.030	6.978 ± 0.030
H-1(D)	3.676 ± 0.025	55.792 ± 0.038	25.018 ± 0.034	7.865 ± 0.016	7.650 ± 0.021
H-2(W)	2.065 ± 0.039	52.964 ± 0.030	23.126 ± 0.018	10.350 ± 0.010	11.495 ± 0.013
H-2(D)	2.227 ± 0.018	52.399 ± 0.034	23.055 ± 0.027	10.673 ± 0.012	11.646 ± 0.014

TABLE-5
COMPARISON OF U, Pu, Cs AND Eu ISOTOPIC RATIOS IN CLADDING SAMPLES

Sample	Atom ratio				Activity ratio	
	$^{235}\text{U}/^{236}\text{U}$	$^{235}\text{U}/^{238}\text{U}$	$^{239}\text{Pu}/^{240}\text{Pu}$	$^{239}\text{Pu}/^{242}\text{Pu}$	$^{134}\text{Cs}/^{137}\text{Cs}$	$^{155}\text{Eu}/^{154}\text{Eu}$
H-1(W)	1.882	0.010	2.702	8.903	0.007	0.196
H-1(D)	1.328	0.008	2.230	7.293	0.003	0.162
H-2(W)	0.985	0.007	2.290	4.608	0.045	0.286
H-2(D)	1.039	0.007	2.273	4.499	0.046	0.271

TABLE-6
DETERMINATION OF U AND ITS ISOTOPES IN CLADDING SAMPLES BY IDMS

Sample	U ($\mu\text{g/g-sample}$)				
	^{234}U	^{235}U	^{236}U	^{238}U	Total
H-1(W)	0.12	4.57	2.45	474.58	481.7 ± 19.0
H-1(D)	0.03	0.68	0.53	90.25	91.5 ± 4.0
H-2(W)	2.34	61.03	62.19	9029.44	9155 ± 275
H-2(D)	0.01	0.35	0.34	49.51	50.2 ± 3.0

TABLE-7
DETERMINATION OF PU AND ITS ISOTOPES IN CLADDING SAMPLES BY IDMS

Sample	Pu (μg/g-sample)					Total
	²³⁸ Pu	²³⁹ Pu	²⁴⁰ Pu	²⁴¹ Pu	²⁴² Pu	
H-1(W)	0.09	4.40	1.64	0.48	0.50	7.1 ± 1.0
H-1(D)	0.01	0.17	0.08	0.02	0.02	0.3 ± 0.03
H-2(W)	4.40	113.35	49.70	22.34	24.91	214.7 ± 21
H-2(D)	0.08	1.78	0.78	0.36	0.40	3.4 ± 0.5

distributed in the interior of the cladding, in addition, the contents of U and Pu deposited on the surface of the cladding are increase with increasing fuel burnup.

Conclusion

An analytical process has been developed for the determination of the U, Pu, Cs and Eu isotopes in the fuel cladding using isotope dilution mass spectrometry and γ -ray spectrometry. Two-step dissolution procedure using HF and aqua regia was very effective for the dissolution of fuel cladding. The U and Pu in the fuel claddings were purely separated without contributions of various isobars by an anion exchange chromatography. The isotopic compositions for U, Pu, Cs and Eu on the surface and in the interior of high burnup fuel cladding, are similar to each other. On the other hand, in the case of those of low burnup fuel cladding, there was a distinct difference between the two values. The U and Pu in the

cladding are mainly present on the surface and only a small amount is distributed in the interior of the cladding, while the Cs and Eu isotopes were distributed similarly on the surface and in the interior of the cladding, regardless of fuel burnup.

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