

# DETERMINATION OF THE TRANSURANIC ELEMENTS INVENTORY IN HIGH BURNUP PWR SPENT FUEL SAMPLES BY ALPHA SPECTROMETRY

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The contents of transuranic elements in high-burnup spent fuel samples were determined. The activity amounts of  $^{238}\text{Pu}$ ,  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$ ,  $^{241}\text{Am}$ ,  $^{244}\text{Cm}$  and  $^{242}\text{Cm}$  were measured by alpha spectrometry using  $^{242}\text{Pu}$  and  $^{243}\text{Am}$  as tracers, respectively. A spike addition method for  $^{237}\text{Np}$  was established by an alpha and gamma spectrometry using  $^{239}\text{Np}$  as a spike after the optimum conditions for the measurements of  $^{237}\text{Np}$  and  $^{239}\text{Np}$ , respectively, were obtained.

A separation system using anion exchange chromatography and diethylhexylphosphoric acid extraction chromatography was applied for the separation of these elements.

This method was applied to high-burnup spent nuclear fuel samples (40~60GWD/MTU). The contents of the transuranic elements were compared with those by ORIGEN-2 code. Measurements and the calculations of the contents of the plutonium isotopes  $^{238}\text{Pu}$ ,  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  agreed to within 10% on average. The contents of  $^{237}\text{Np}$  agreed to within approximately 5% except for one instance of a calculation, while those of  $^{241}\text{Am}$ ,  $^{244}\text{Cm}$  and  $^{242}\text{Cm}$  showed higher values by approximately 19%, 35% and 14% on average, respectively, compared to the calculations according to the burnup.

**KEYWORDS** : Transuranic Elements, High-burnup Spent Fuels, Inventory of Transuranic Elements, Alpha Spectrometry, Isotopic Analysis, Spike Addition Method

## 1. INTRODUCTION

Determination of transuranic elements such as U, Pu, Np, Am and Cm in spent nuclear fuels is of importance for a fuel characterization, evaluation of a burnup credit, and burnup determination of spent nuclear fuels. Additionally, the exact amount of the actinide elements, as the major elements of a source term, of the spent nuclear fuels is also used for a code verification that predicts the amount of the nuclides produced or decayed during a neutron irradiation. For the determination of the elemental components in spent nuclear fuel samples using a chemical method, a tracer is generally used depending on the elements and determination method. Accordingly, a special precaution is required in the selection of an appropriate tracer, as spent nuclear fuel samples contain a variety of elements and various levels of activities compared to environmental samples. For example,  $^{237}\text{Np}$  emits relatively low alpha activity due to its long half life ( $2.14 \times 10^6$  y) while the isotopes of Am, Cm and Pu emit relatively high activities. Consequently, a simultaneous determination of

these transuranic nuclides by alpha spectrometry with a single run taking only one sample is limited due to the different activity ratios between each nuclide, as mentioned above.

In this work, high-burnup PWR spent fuel samples (36.97 ~ 62.85 GWD/MTU) were analyzed. The contents of transuranic elements were compared with those calculated by the ORIGEN-2 code. Alpha spectrometry was applied for the determination of the elements using a tracer or a spike. The isotopes determined in this work were  $^{238}\text{Pu}$ ,  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$ ,  $^{237}\text{Np}$ ,  $^{241}\text{Am}$ ,  $^{244}\text{Cm}$  and  $^{242}\text{Cm}$ . In particular, for  $^{237}\text{Np}$ , a spike addition method as an isotope dilution technique [1] was applied using  $^{239}\text{Np}$  as a spike after verification of the method because the spent nuclear fuel samples contain a considerable amount of  $^{239}\text{Np}$ .

Other nuclides were determined by alpha spectrometry using  $^{242}\text{Pu}$  and  $^{243}\text{Am}$  as the tracers.

Generally, the recommended tracers [2] are  $^{243}\text{Am}$  for  $^{241}\text{Am}$ ,  $^{248}\text{Cm}$  for  $^{244}\text{Cm}$  and  $^{242}\text{Cm}$ ,  $^{242}\text{Pu}$  for  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$ , and  $^{239}\text{Np}$  [3],  $^{236}\text{Np}(t_{1/2}, 5000\text{y})$  [4],  $^{235}\text{Np}(t_{1/2}, 396.1\text{d})$  [5],  $^{242}\text{Pu}$  [6] for  $^{237}\text{Np}$ . The tracers,  $^{248}\text{Cm}$  and  $^{235}\text{Np}$  or  $^{236}\text{Np}$ ,

were not available for this study; so  $^{243}\text{Am}$  and  $^{239}\text{Np}$  were used for the curium isotopes [7] instead and  $^{237}\text{Np}$  as the tracer and spike, respectively.

The separation method used was anion exchange chromatography [2] and/or diethylhexylphosphoric acid (HDEHP) extraction chromatography [8]. The separated elements were electrodeposited, which was followed by alpha and gamma spectrometry. Finally, the contents of the transuranic elements were compared with those by calculations using ORIGEN-2 code.

## 2. EXPERIMENTS

### 2.1 Reagents and Apparatus

An anion exchanger was used for the separation of the transuranic elements (AGMP-1 x 8, 100-200 mesh size, Boi-Rad Laboratories, USA). A glass column (inner diameter 7 mm x height 70 mm, Sigma Co) filled with the anion exchanger was used. A disposable polyethylene column (inner diameter 4 mm x height 48 mm) filled with an adsorbent (diethylhexylphosphoric acid coated onto styrenedivinylbenzene copolymer, 100-200 mesh size, 2.08 mmole HDEHP/g) was used for the separation of Am and Cm. Diethylhexylphosphoric acid (>95%, Aldrich Chem. Co, USA), diethylenetriaminetetraacetic acid (DTPA)(97%, Aldrich Chem. Co, USA) and lactic acid (LA)(85-90%, Tedia Co, USA) were used for the adsorbent and eluents for the separation of Am and Cm, respectively. Amberlite XAD-XVI copolymer as the supporting material for the adsorbent was the product of the Merck Company of Germany. The standard solutions of  $^{243}\text{Am}$  (37.52 KBq  $\pm$ 3% uncertainty, 4.961 g-soln, Nov.1 1991) and  $^{242}\text{Pu}$  (25.67 Bq/g,  $\pm$ 0.72% uncertainty, 5.5 g-soln, Aug. 1, 1999) as the tracers were the products of the North American Scientific Inc (Model Cal 3000) and NBL(CRM) of the USA, respectively. Standard solutions of  $^{241}\text{Am}$  (417 KBq,  $\pm$ 2.35% uncertainty, 5.0379 g-soln, Aug. 1, 1994),  $^{244}\text{Cm}$  (370 KBq,  $\pm$ 1.67% uncertainty, 5.297 g-soln, Sep. 1, 1994) and  $^{239}\text{Pu}$  (41.59 KBq,  $\pm$ 4.01% uncertainty, 5.19 g-soln, NoV. 1, 1995) were purchased from the North American Scientific Inc. of the USA. The standard material of  $^{237}\text{Np}$  (832 KBq/g,  $\pm$ 3% impurities, 1.066 g-soln) was obtained from the Damri Company (CEA) of France. A standard alpha source mixed with  $^{241}\text{Am}$ ,  $^{244}\text{Cm}$  and  $^{239}\text{Pu}$  at nearly the same ratio ( $3.28 \times 10^5$  dpm, July 16, 1986, Amersham, Co, UK) was used for the energy and efficiency calibration with alpha spectrometry. Standard solutions (1,000mg/L,  $\pm$ 3% uncertainty) of lanthanides and inactive fission products used for preparing a synthetic solution of the spent nuclear fuel samples were the products of Spex Co of the USA. A standard solution of  $^{152}\text{Eu}$  (45700 Bq/mL, January 1, 1991, code no EFY.64, Amersham Co, UK) was used for an energy calibration of the gamma spectrometer.

The alpha spectrometer with a silicon surface detector

of 300 mm<sup>2</sup> and the gamma spectrometer were the products of the EG&G ORTEC company of the USA. Total alpha counting was conducted by a Gas Proportional Counting System (LB 5100, Tennelec Co, USA). The mass spectrometer used for the measurement of  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  was the Finnigan Mat 262 of the Finnigan Mat Company of Germany. The electrodeposition system was composed of a polyethylene cell (inner diameter 20mm x height 80mm), a planchet disc of stainless steel (diameter 1 inch x thickness 0.5mm) and a Pt electrode (diameter 1 mm x length 100 mm). NaHSO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub> used as an electrolyte were the products of an extra pure grade of the Junsei Company of Japan and GR of the Merck company of Germany, respectively.

### 2.2 Spike Addition Method for $^{237}\text{Np}$

For the determination of  $^{237}\text{Np}$  using a spike addition method, preliminary work for the gamma spectrometry was performed to find the optimum condition for measuring the  $^{239}\text{Np}$ . An appropriate amount of  $^{239}\text{Np}$  ( $^{243}\text{Am}$  standard solution) was dried onto a planchet from 1.8 Bq to 30 Bq. The activities of  $^{239}\text{Np}$  and  $^{243}\text{Am}$  were measured using gamma spectrometry and gross alpha counting, respectively, in order to obtain the correction factor for the measurement of each nuclide. Two gamma energies of 228.19 KeV and 277.6 KeV were selected for the measurement of  $^{239}\text{Np}$ . The gamma activity of the  $^{239}\text{Np}$  was measured and the alpha activity of the  $^{243}\text{Am}$  was then measured by gross alpha counting for the same planchet co-dried onto as  $^{239}\text{Np}$ . The correction factor for  $^{239}\text{Np}$  was determined from the measurement values and the added values.

Prior to the determination of  $^{237}\text{Np}$  in spent fuel samples, the recovery yields and precisions for isotope dilution alpha (gamma) spectrometry (IDAS) as a spike addition method were measured using standard solutions for the validation of the method. Two types of "samples" were prepared. A "sample" solution containing an appropriate amount of  $^{237}\text{Np}$  (0.1 ~ 5 Bq) and approximately 30 Bq of  $^{239}\text{Np}$  was prepared, and a "spiked sample" was prepared by mixing the "sample" solution and a "spike" solution. Approximately 15 Bq of  $^{239}\text{Np}$  was added into the sample solution as a spike. Appropriate amounts of  $^{237}\text{Np}$  and  $^{239}\text{Np}$  were dried together onto a planchet, and the activity of each nuclide in the "sample" and "spiked sample" was measured in order to obtain the isotope ratios by alpha and gamma spectrometry for  $^{237}\text{Np}$  and  $^{239}\text{Np}$ , respectively. Finally, the amount of  $^{237}\text{Np}$  was calculated using the related equation (1) [1]. The recovery yields and precisions were also obtained.

$$C_x = C_t \left( \frac{m_t}{m_x} \right) \left( \frac{M_x}{M_t} \right) \left( \frac{R_t - R_m}{R_m - R_x} \right) \left( \frac{\sum_x Ri}{\sum_t Ri} \right) \quad (1)$$

Here,  $C_x$  denotes the total concentration of Np in the

sample solution,  $C_i$  is the total concentration of Np in the spike solution,  $m_i$  is the weight of the spike solution,  $m_x$  is the weight of the sample solution,  $M_x$  is the average atomic weight of Np in the sample solution,  $M_i$  is the average atomic weight of Np in the spike solution,  $R_i$  is the isotope ratio of  $^{237}\text{Np}/^{239}\text{Np}$  in the spike solution,  $R_m$  is the isotope ratio of  $^{237}\text{Np}/^{239}\text{Np}$  in the spiked sample solution,  $R_x$  is the isotope ratio of  $^{237}\text{Np}/^{239}\text{Np}$  in the sample solution,  $\sum_x R_i$  is the sum of isotope ratios of Np in the sample solution ( $^{237}\text{Np}/^{239}\text{Np} + ^{239}\text{Np}/^{239}\text{Np}$ ) and  $\sum_i R_i$  is the sum of isotope ratios of Np in the spike solution ( $^{237}\text{Np}/^{239}\text{Np} + ^{239}\text{Np}/^{239}\text{Np}$ ).

### 2.3 Sample Preparation

Seven high-burnup PWR spent nuclear fuel samples from the Youngkwang unit 1 (4 samples) and the Uljin unit 2 (3 samples) in Korea were taken (Table 1). The burnup of the samples ranged from 36.97 to 62.85 GWD/MTU and the cooling times were distributed from 3.1 to 5.1 years, as shown in Table 1. The fuel samples of ~0.5 g were dissolved with (1+1) nitric acid in a hot cell. A mother solution was diluted to an appropriate concentration. An appropriate amount of sample solution was sent to a glove box by a pneumatic transfer.

### 2.4 Determination of Transuranic Elements in Spent Fuel Samples

For the determination of  $^{237}\text{Np}$ , two measurements for one sample were conducted by taking two identical samples ("sample" and "spiked sample") equivalent to ~100  $\mu\text{g}$  U each. Approximately 30 ~ 60 Bq of  $^{239}\text{Np}$  was added to one ("a spiked sample"). The two sample solutions were dried on a hot plate and the residues were dissolved with 1 ~ 2 mL of C-HNO<sub>3</sub>. The sample matrix was transformed to nitrate salts in one or two nitric acid treatments. Finally, the residues were dissolved with 1 mL of 10 M HCl and kept for the next step. The two samples were applied

separately to each anion exchange column (Fig. 1). The  $^{239}\text{Np}$  and  $^{237}\text{Np}$  in the "sample" and "spiked sample" were measured by gamma spectrometry and alpha spectrometry, respectively, after separation followed by electrodeposition. In particular, the gamma activity of  $^{239}\text{Np}$  was measured

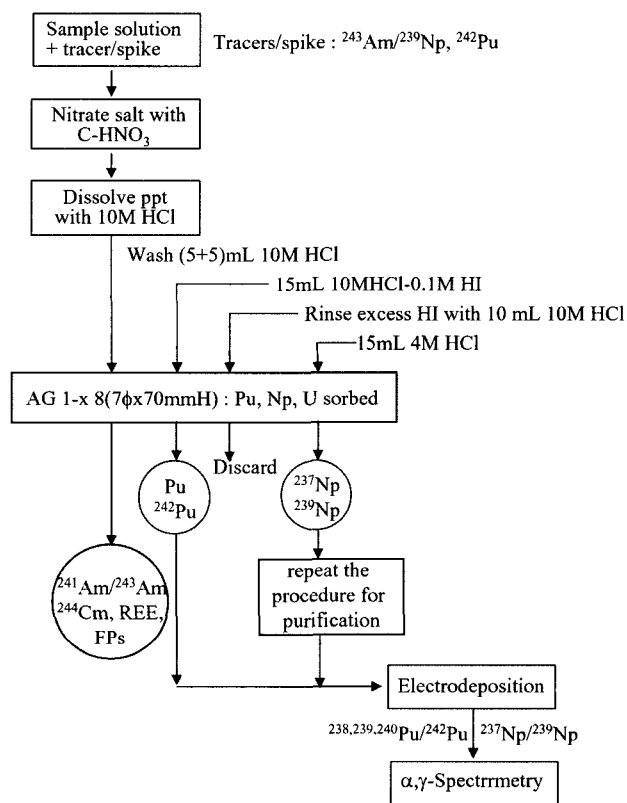


Fig. 1. Sequential Separation of Transuranic Elements in Spent Fuel Samples.

Table 1. Sample History of Spent Nuclear

Sample	Discharged	Measurement	Cooling time (d)	GWD/MtU*
SF-1	2003-05-10	2006-06-20	1137	57.37
SF-2	2003-05-10	2006-06-20	1137	43.47
SF-3	2003-05-10	2006-09-13	1222	36.97
SF-4	2003-05-10	2006-09-13	1222	49.01
SF-5	2001-05-15	2006-06-20	1862	62.85
SF-6	2001-05-15	2006-06-20	1862	59.72
SF-7	2001-05-15	2006-06-20	1862	47.93

\*<sup>148</sup>Nd method, <sup>235</sup>U initial conc. 4.201%

as soon as possible after separation from the spent fuel samples due to its short half life (2.35 d). The alpha activities of  $^{237}\text{Np}$  in the spent fuel samples were measured at 4.79 MeV using the same planchet co-electrodeposited onto as  $^{239}\text{Np}$ . The content of  $^{237}\text{Np}$  was calculated using the ratios of  $^{237}\text{Np}/^{239}\text{Np}$  in the “sample” and “spiked sample”, respectively.

For the determination of Pu, Am and Cm, a small sample size equivalent to approximately 0.1  $\mu\text{g}$  of U was taken after considerable dilution of the sample solution. Approximately 15 Bq of  $^{243}\text{Am}$  and 1.54 Bq of  $^{242}\text{Pu}$  as tracers were added to the sample solution.  $^{243}\text{Am}$  standard solution was directly used as a tracer without milking  $^{239}\text{Np}$  from it, as mentioned above. Both anion exchange chromatography (Fig. 1) and HDEHP extraction chromatography (Fig. 2) were used in a series for the separation of Pu, and Am and Cm. The Am and Cm were eluted together with 6 mL of 0.05 M DTPA-0.5 M lactic acid with successive additions of 3 mL each on an extraction column after elution through the an anion exchange column. The lanthanides as well as Mo and Zr are then eluted with 5 mL of 6 M  $\text{HNO}_3$  after Am and Cm are eluted [8]. However, this step was omitted in this work. The alpha activities of the plutonium isotopes were measured at 5.5 MeV of  $^{238}\text{Pu}$ , 5.16 MeV of  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$ , and 4.9 MeV of  $^{242}\text{Pu}$ . The alpha activities for  $^{241}\text{Am}$ ,  $^{243}\text{Am}$ ,  $^{244}\text{Cm}$  and  $^{242}\text{Cm}$  were measured at 5.48 MeV, 5.27MeV, 5.81 MeV and 6.11 MeV, respectively, after electrodeposition [9,10]. The recovery yields of  $^{242}\text{Pu}$  and  $^{243}\text{Am}$  were applied for the plutonium, and the americium and curium isotopes, respectively.

### 3. RESULT AND DISCUSSION

#### 3.1 Validation of the Method

The isotopes of  $^{239}\text{Pu}$ ,  $^{237}\text{Np}$  and  $^{241}\text{Am}$  were selected as the representative isotopes for the verification of individual separations with anion exchange chromatography and HDEHP extraction chromatography according to the procedure described in Figs. 1 and 2.  $^{241}\text{Am}$ , Dy and Nd were also tested for the separation of Am and Cm from lanthanides and other fission products. A good resolution was obtained between the two elements of  $^{237}\text{Np}$  and  $^{239}\text{Pu}$ . The Am was also purely separated from Dy and Nd. The Cm was reported to elute slightly behind the Am on the same column [7,8].

Before being placed in a spent fuel sample, a synthetic sample solution was prepared. An aliquot of the synthetic sample solution containing  $\sim 100\mu\text{g}$  U was taken and appropriate amounts (1  $\sim$  50 Bq of each nuclide) of  $^{241}\text{Am}$ ,  $^{244}\text{Cm}$ ,  $^{237}\text{Np}$ ,  $^{239}\text{Pu}$ ,  $^{243}\text{Am}$ ,  $^{239}\text{Np}$  and  $^{242}\text{Pu}$  were added to the sample solution. These elements were separated according to the procedures shown in Figs. 1 and 2 and were determined by alpha spectrometry and gamma spectrometry in the same manner as that used in the experimental section.

The recovery yields from the synthetic solution were found to range from 80.9% to 93.7% with a precision of 2.3  $\sim$  11.4% (1S, n=3) for the seven nuclides. The activity of  $^{239}\text{Np}$  was measured by gamma spectrometry 5 or 6 hours after separation from  $^{243}\text{Am}$ , and the measured activity was also corrected for the decay time. The recovery yields of  $^{241}\text{Am}$  and  $^{244}\text{Cm}$  from the synthetic sample solution agreed to within 5% using  $^{243}\text{Am}$  as a tracer for both nuclides and were also reported to be in agreement to within 5% for another work with radwaste samples [7]. Consequently, in this work,  $^{243}\text{Am}$  used as a tracer was shown to be valid for the determination of  $^{244}\text{Cm}$  and  $^{242}\text{Cm}$ .

The standard solution of  $^{243}\text{Am}$  contains an equal amount of  $^{239}\text{Np}$ , as  $^{243}\text{Am}$  decays to  $^{239}\text{Np}$  by an alpha emission and reaches a secular equilibrium state after an equilibrium time, resulting in an equal amount of produced  $^{239}\text{Np}$ . Accordingly, gamma spectrometry for  $^{239}\text{Np}$  was studied as  $^{239}\text{Np}$  only emits pure low gamma energies less than 300 KeV. An optimum measurement condition by gamma spectrometry was obtained after the correction factor was determined as a function of the  $^{239}\text{Np}$  amount. In this work, the selected two gamma energies (228.07 Kev/277.86 Kev) for an efficiency calibration showed relatively high energies and high branching ratios (12  $\sim$  14.1%) when compared to the other gamma energies (14.3  $\sim$  334.3 KeV). The ratio of the measurement value over the added value ( $^{239}\text{Np}_{\text{meas}}/^{239}\text{Np}_{\text{add}}$ ) decreased to 1.06 as the amount of  $^{239}\text{Np}$  increased from 1.8 Bq to 30 Bq, as shown in Fig. 3. The higher ratios ( $>1$ ) of  $^{239}\text{Np}$  were presumed to result from a higher background effect due to its lower gamma energies. However, the exact

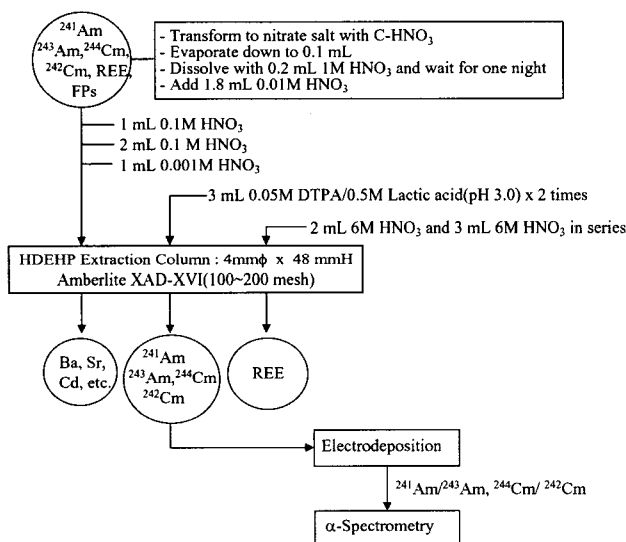


Fig. 2. Separation of Am and Cm from Fission Products in a Spent Nuclear Fuel Sample

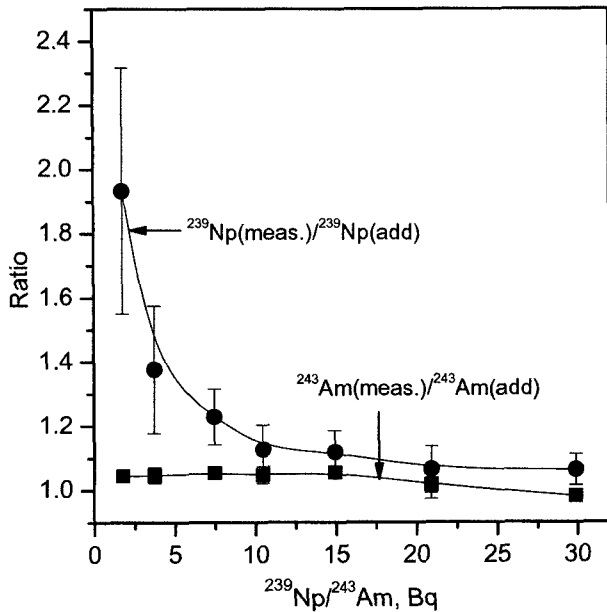


Fig. 3. Correction Factors for the Measurement of  $^{239}\text{Np}$  and  $^{243}\text{Am}$  in  $^{243}\text{Am}$  Standard Solution after Dried onto a Planchet.  $^{239}\text{Np}$ ; Gamma Spectrometry,  $^{243}\text{Am}$ ; Gross Alpha Counting, Error Bar; 1S

reason was not identified. The ratio of  $^{239}\text{Np}$  at the range from 15 Bq and above showed a plateau. Thus, the correction factor used in this experiment was 1.06. In particular, in this work, the uncertainty caused by gamma spectrometry appears insignificant, as the amount of the  $^{239}\text{Np}$  measured in the spent nuclear fuel samples was nearly 200 Bq, which is much higher than the 30 Bq tested previously. Therefore, the measurement was stabilized considerably. In the case of  $^{243}\text{Am}$ , the ratio of the alpha activities of the measurement over the addition were nearly uniform regardless of the amount of  $^{243}\text{Am}$ .

The spike addition method used for  $^{237}\text{Np}$  in this work was modified from isotope dilution mass spectrometry (IDMS)[1]. In this method, alpha and gamma spectrometry were used instead of a mass spectrometry as the detection methods for  $^{237}\text{Np}$  and  $^{239}\text{Np}$ , respectively.

As a subsequent step, the application of isotope dilution alpha (gamma) spectrometry to the spent fuel samples was verified using the standard solutions of  $^{237}\text{Np}$  and  $^{239}\text{Np}$ , respectively, as mentioned in the previous section. The amounts of  $^{237}\text{Np}$  in "sample" solution were calculated by Eq. (1). As shown in Table 2, the recovery yields are nearly quantitative for the range of the  $^{237}\text{Np}$  amount tested. The precision (RSD) gradually worsened from approximately 5% to 30% as the amount of  $^{237}\text{Np}$  decreased from 5 Bq to 0.1 Bq. However, the precisions were nearly 20% and less than 10% at levels over 1 Bq and 2 Bq of  $^{237}\text{Np}$ , respectively. Thus, in this work, the precision associated

Table 2. Recovery Yield and Precision for the Measurement of  $^{237}\text{Np}$  by Isotope Dilution Alpha (Gamma) Spectrometry

$^{237}\text{Np}(\text{Bq})$		Recovery (%)
Added	Meas.±1S(n=3)	
0.10	0.10±0.031	100 ±31
1.00	1.01 ±0.23	101.0 ±22.7
2.00	1.98 ±0.16	98.7 ±8.1
4.16	3.97	95.5
5.00	5.22 ±0.20	104.4 ±3.8

\*A spike: 15 Bq of  $^{239}\text{Np}$ , Sample:  $^{237}\text{Np}$  + 30 Bq of  $^{239}\text{Np}$   
 \* $^{237}\text{Np}$ ; alpha spectrometry,  $^{239}\text{Np}$ ; gamma spectrometry

with the determination of  $^{237}\text{Np}$  in the spent fuel samples was presumed to be 20% or less, as the alpha activities of  $^{237}\text{Np}$  in the sample measurements were in the region of 1 Bq.

In this work, the uncertainties associated with the determinations of transuranic elements in the spent fuel samples were presumed to be 25% or less as the expanded standard uncertainty, as the uncertainties were previously evaluated for  $^{241}\text{Am}$  including other transuranic elements in radioactive waste samples from nuclear power plants [11] according to the EURACHEM guide [12] in the laboratory of the authors before and the uncertainties in those samples (~2 Bq per sample) were about 25%. The activities of  $^{241}\text{Am}$  in the spent fuel samples in this work were higher (~10 Bq per sample) than the radioactive waste samples. Hence, the uncertainties associated with this work might be lower than those with radioactive waste samples due to the higher activity. For this reason, the uncertainty evaluated for the radioactive waste samples could be applied in this work as a guideline as the analytical method (except for that of  $^{237}\text{Np}$ ) was nearly identical for the two types of samples.

### 3.2 Determination of the Transuranic Elements in Spent Fuel Samples

In the spent nuclear fuel samples, the amount of transuranic nuclides produced during neutron irradiation were estimated by the ORIGEN-2 code [13]. Table 3 shows the amount of each nuclide calculated in the spent nuclear fuels based on a burnup of 50 GWD/MTU. According to Table 3, two different approaches were adopted depending on the nuclides to be determined. For the determination of  $^{237}\text{Np}$ , a relatively large sample size (~100 µg U) was taken using  $^{239}\text{Np}$  as a spike, as a spent nuclear fuel sample itself includes a considerable amount of  $^{239}\text{Np}$ , as outlined in Table 3. Thus, adopting a small amount of a sample as an alternative in order to reduce

**Table 3.** Estimated Amounts of Transuranic Elements in a Spent Nuclear Fuel Sample Using the ORIGEN-2 Code

Unit \ Nuclide	<sup>240</sup> Pu	<sup>239</sup> Pu	<sup>238</sup> Pu	<sup>242</sup> Pu	<sup>237</sup> Np	<sup>239</sup> Np	<sup>241</sup> Am	<sup>243</sup> Am	<sup>244</sup> Cm	<sup>242</sup> Cm
g/g <sup>238</sup> U	2.91 E-03	6.31 E-03	3.41 E-04	9.32 E-04	8.4 E-04	2.03 E-10	7.9 E-04	2.36 E-04	6.83 E-05	3.38 E-09
Spec. act. (Bq/ng)	83.96	2.298	643.8	0.144	0.0261	7.85 E+06	127.16	6.81	2.99 E+03	1.2 E+05
Bq/0.1 mg <sup>238</sup> U	2.45 E+03	1.45 E+03	2.2 E+04	1.34 E+01	2.19 E+0	1.59 E+02	1.004 E+04	1.61 E+02	2.05 E+04	4.09 E+01
Bq/0.1 μg <sup>238</sup> U	2.44	1.45	21.97	0.0134	0.0022	0.16	10.04	0.16	20.5	0.041
Spike/Tracer(Bq)				1.54		30		15		

\*Spent nuclear fuel: 50GWD/MTU, 10y cooling

the amount of <sup>239</sup>Np is also limited due to the low alpha activity of <sup>237</sup>Np. The activities of <sup>239</sup>Np and <sup>237</sup>Np in the “sample” and “spiked sample” were measured after separations and electrodepositions followed by gamma and alpha spectrometry, respectively, as mentioned earlier.

Finally, the activity of <sup>237</sup>Np in a sample was calculated using Eq. (1).

The <sup>237</sup>Np fraction eluted from the anion exchange column was purified by repeating the full procedure an additional time, and the high plutonium peaks in the Np fraction before purification were considerably reduced after purification. The plutonium peaks in the Np fraction could be reduced more by allowing them to stand for more than 20 min to reduce the Pu<sup>4+/6+</sup> to Pu<sup>3+</sup> fully ahead of the Np elution in the separation procedure.

For other nuclides such as <sup>238</sup>Pu, <sup>239</sup>Pu and <sup>240</sup>Pu, <sup>241</sup>Am, <sup>244</sup>Cm and <sup>242</sup>Cm, the tracers of <sup>242</sup>Pu and <sup>243</sup>Am were used. A small sample size containing approximately 0.1 μg U was taken after a considerable dilution of the sample solution so that the <sup>243</sup>Am and <sup>242</sup>Pu originally present in the sample solution would not interfere adversely with the same nuclides added as tracers. 1.54 Bq of <sup>242</sup>Pu and 15 Bq of <sup>243</sup>Am were added to the samples as tracers. This small sample size was presumed originally to contain approximately 0.013 Bq of <sup>242</sup>Pu and 0.16 Bq of <sup>243</sup>Am, as shown in Table 3. Accordingly, a nearly 1% error rate caused by the use of tracers was expected in the determination of Am, Cm and Pu. In Fig. 4, the alpha spectrum of the plutonium isotopes in a sample (SF-1) is shown. The three peaks of <sup>238</sup>Pu, <sup>239/240</sup>Pu and <sup>242</sup>Pu were clearly resolved. A small peak of <sup>244</sup>Cm was also observed. This small peak of <sup>244</sup>Cm in the plutonium fraction implies that a large peak of <sup>238</sup>Pu(5.5 MeV) was not contaminated by the <sup>241</sup>Am (5.48 MeV), as the peak of <sup>244</sup>Cm is generally much higher than <sup>241</sup>Am or is similar to that of spent fuels, as shown in Fig. 5 and Table 3. In Fig. 5, the spectrum of the Am and Cm isotopes in a sample (SF-1) was expressed as a representative. The peaks of the four nuclides were clearly

resolved. The peak of <sup>241</sup>Am might experience interference from <sup>238</sup>Pu if the plutonium is contaminated. However, in this sample it was confirmed that the fraction of americium and curium eluted together was not contaminated by plutonium as the peak of <sup>239/240</sup>Pu was not observed at 5.16 MeV of the <sup>239/240</sup>Pu. The peak of <sup>243</sup>Am added as a tracer was also clearly observed. The peaks in Figs. 4 and 5 were extremely sharp and highly resolved when compared to those of the alpha spectra obtained with only dryness and not electrodeposition, as in a different study [14]. The amounts of <sup>244</sup>Cm and <sup>242</sup>Cm were also determined using <sup>243</sup>Am as a tracer, as mentioned above.

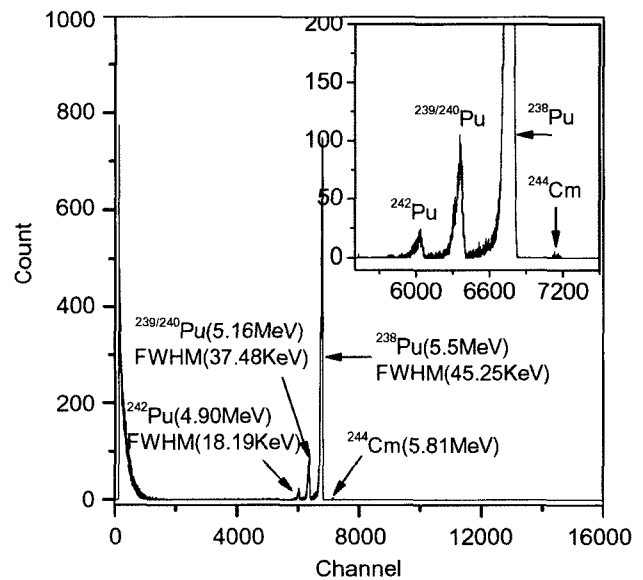


Fig 4. Alpha Spectrum of Plutonium Isotopes Separated and Electrodeposited in Spent Nuclear Fuel Sample. Sample : SF-1, Tracer; <sup>242</sup>Pu 1.54 Bq, Counting Time; 5000 sec

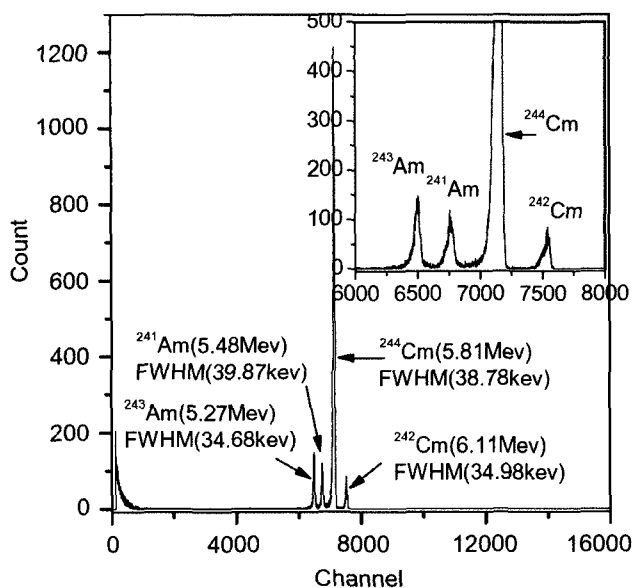


Fig 5. Alpha Spectrum of  $^{241}\text{Am}$ ,  $^{244}\text{Cm}$  and  $^{242}\text{Cm}$  Separated and Electrodeposited in Spent Nuclear Fuel Sample. Sample : SF-1, Tracer,  $^{243}\text{Am}$  15Bq, Counting Time; 5000 sec

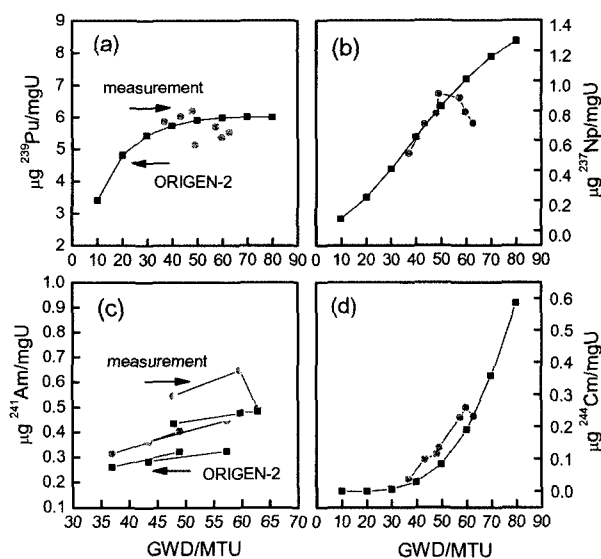


Fig. 6. Correlation of transuranic elements between measurements and calculations by ORIGEN-2 code as a function of burnup. (a)  $^{239}\text{Pu}$ , (b)  $^{237}\text{Np}$ , (c)  $^{241}\text{Am}$ : cooling time (day); 1137(left), 1222(middle), 1862(upper), (d)  $^{244}\text{Cm}$

### 3.3 Correlation with ORIGEN-2 Code

In Table 4, the amounts of each nuclide determined from the spent nuclear fuel samples are shown. They were compared with those calculated by the ORIGEN-2 code as the percentage of differences between the measurements and the calculations for each nuclide and each sample. Fig. 6 shows the correlations between the measurement and the calculations as a function of burnup at a range of approximately 40 ~ 60 GWD/MTU for  $^{239}\text{Pu}$ ,  $^{237}\text{Np}$ ,  $^{241}\text{Am}$ , and  $^{244}\text{Cm}$ . As shown in Table 4 and Fig. 6(a), the contents of  $^{238}\text{Pu}$ ,  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  largely agreed with those by the ORIGEN-2 code to within -10.2%, 1.1% and -4.6% (average values), respectively. The Pu isotope data reported [15] from the Takahama-3 reactor also agreed well with the calculations to within 13.3% for a burnup of 30 ~ 47.25 GWD/MTU [15]. For the low burnup PWR fuels (~ 5 GWD/MTU), the plutonium isotope data (Pu/U) were also found to agree to within -15% with those by the ORIGEN-2 code, except for  $^{238}\text{Pu}$  (-31.1%)[16]. This highly biased  $^{238}\text{Pu}$  datum from the calculation appeared to be due to  $^{238}\text{U}$  determined by mass spectrometry. Accordingly, the alpha spectrometry used in this work is advantageous for the measurement of  $^{238}\text{Pu}$ . For the measurement of the individual activity levels of  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$ , the total alpha activity of  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  measured at 5.16 MeV was divided for each nuclide by applying the specific activity and isotope ratio measured by mass spectrometry. In Fig. 6(b), the correlation of  $^{237}\text{Np}$  between the measurement and the calculation is shown. The measurement values

agreed to within 5.4% with those by the calculations except for one data item (48.6%) on average as a function of the burnup. For the high-burnup PWR spent fuels from the Takahama-3 reactor, the measurements were found to be in good agreement to within a 4% (30 ~ 47.25 GWD/MTU) difference with the calculation (SAS2H code) and showed lower values in a range of 34.2 ~ 71.8% (7 ~ 28.9 GWD/MTU) compared to the calculations [15].

Literature regarding  $^{237}\text{Np}$  determined in MOX fuel irradiated up to 120 GWD/MTU in the Mark-II core of JOYO in Japan has been reported [17]. The content of  $^{237}\text{Np}$  was also compared with that calculated by ORIGEN-2. The data from samples irradiated at the top and bottom ends of the axial arrangement of a pin deviate greatly from the calculation values (expressed as only a graph). However, the content of  $^{237}\text{Np}$  from the samples irradiated at the core center agrees well with the calculation, with some uncertainties.

In this study, the activity of  $^{237}\text{Np}$  was excessively low compared to that of  $^{239}\text{Np}$  in the spent fuel samples. Accordingly, the considerable difference in the activity amount between  $^{237}\text{Np}$  and  $^{239}\text{Np}$  can cause errors in the calculation of the activity ratio ( $^{237}\text{Np}/^{239}\text{Np}$ ) used for the isotope dilution equation (1).

In Fig. 6(c), the amount of  $^{241}\text{Am}$  is also expressed as a function of the burnup. The measurement for  $^{241}\text{Am}$  was corrected according to that contributed by  $^{241}\text{Pu}$  as a function of the cooling time after the fuels were discharged from the reactor. The samples taken in this study had three different cooling times (1137, 1222 and

**Table 4.** Comparison of the Percentage Differences Between the Measurements and Calculations for the High-Burnup Spent Fuel Samples (Unit: µg/mgU)

Nuclide		<sup>238</sup> Pu			<sup>239</sup> Pu			<sup>240</sup> Pu		
Sample	GWD/MTU	meas.	cal.	diff(%)	meas.	cal.	diff(%)	meas.	cal.	diff(%)
SF-3	36.97	0.197	0.172	-12.5	5.863	5.600	-4.5	2.134	2.194	2.8
SF-2	43.47	0.337	0.251	-25.5	6.026	5.696	-5.5	2.753	2.474	-10.1
SF-7	47.93	0.366	0.311	-15.0	6.191	5.731	-7.4	2.861	2.638	-7.8
SF-4	49.01	0.346	0.326	-5.7	5.132	5.737	11.8	2.895	2.674	-7.6
SF-1	57.37	0.511	0.446	-12.8	5.698	5.769	1.2	3.103	2.912	-6.1
SF-6	59.72	0.532	0.481	-9.6	5.363	5.773	7.6	3.025	2.965	-2.0
SF-5	62.85	0.481	0.527	9.5	5.529	5.775	4.5	3.067	3.027	-1.3
Aver ± 1S				-10.2 ± 10.6			1.1 ± 7.3			-4.6 ± 4.6

Nuclide		<sup>238</sup> Pu			<sup>239</sup> Pu			<sup>240</sup> Pu		
Sample	GWD/MTU	meas.	cal.	diff(%)	meas.	cal.	diff(%)	meas.	cal.	diff(%)
SF-3	36.97	0.514	0.556	8.21	0.314	0.261	-16.9	0.0373	0.0175	-53.2
SF-2	43.47	0.708	0.692	-2.27	0.363	0.284	-21.8	0.0984	0.0438	-55.5
SF-7	47.93	0.778	0.784	0.76	0.545	0.435	-20.1	0.1142	0.0711	-37.7
SF-4	49.01	0.909	0.806	-11.38	0.403	0.323	-19.9	0.1346	0.0790	-41.3
SF-1	57.37	0.883	0.967	9.55	0.447	0.325	-27.3	0.2294	0.1589	-30.7
SF-6	59.72	0.791	1.009	27.54	0.647	0.477	-26.3	0.2604	0.1880	-27.8
SF-5	62.85	0.714	1.061	48.64*	0.496	0.483	-2.5	0.2321	0.2317	-0.2
Aver ± 1S				5.4 ± 13.25			-19.3 ± 8.3			-35.2 ± 18.6

\*Omitted for Statistics

Nuclide		<sup>238</sup> Pu		
Sample	GWD/MTU	meas.	cal.	diff(%)
SF-3	36.97	0.00018	0.00017	-8.2
SF-2	43.47	0.0002	0.00022	13.5
SF-7	47.93	0.00039	0.00026	-35.1
SF-4	49.01	0.00038	0.00026	-29.8
SF-1	57.37	0.00036	0.00030	-16.5
SF-6	59.72	0.00042	0.00033	-22.1
SF-5	62.85	0.00034	0.00034	-0.1
Aver ± 1S				-14.0 ± 17.1

1862 days) (Table 1). The amount of <sup>241</sup>Am increased as the burnup increased. The increasing trends differed slightly from each other depending on the cooling time. However, these trends were similar between the measurements and

the calculations, as shown in Fig. 6(c). The average value of <sup>241</sup>Am for the measurement data was found to be approximately 19% higher than that for the calculations. For the high-burn fuels of 30 ~ 47.25 GWD/MTU from the Takahama-3 reactor, the <sup>241</sup>Am data were found to be lower in a range of 5 ~ 26.4% compared to the calculations [15]. The rationale for these higher values of <sup>241</sup>Am in this study was not identified. In Figs 6(d), the correlation of <sup>244</sup>Cm between the measurement data and the calculations is shown as a function of the burnup. The increasing trend of <sup>244</sup>Cm was similar to that in the calculations. However, the measurement showed nearly 35% higher values than the calculation, and the percentage of the difference between the measurements and the calculations decreased from 55% to 0.2% as the burnup increased. In the correlation of <sup>242</sup>Cm between the measurement and the calculations shown in Table 4, the measurement showed approximately 14% higher values than the calculation. For the high-burnup fuels of 30 ~ 47.25 GWD/MTU from the Takahama-3 reactor, the data of <sup>244</sup>Cm and <sup>242</sup>Cm were also found to be in good agreement to within 12.7% with the calculations. However, for the samples of 24 ~ 36.69 GWD/MTU, the



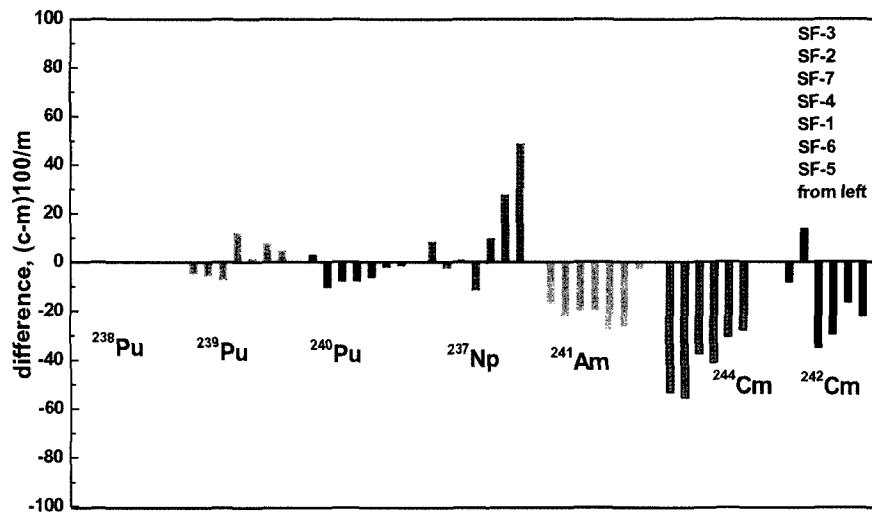


Fig 7. Comparison of Percentage Differences Between Measurements and Calculations for High Burnup Spent Fuel Samples

measurements were found to be higher by as much as 47.7% compared to the calculations. In Fig. 7, the percentage difference between the measurements and the calculations is shown for the isotopes and samples tested in this study. In summary, the amounts of plutonium isotopes were in good agreement to within 10% with those by the calculations. However, the isotopes of Am and Cm showed higher values in a range of 14 ~ 35%, and the contents of the <sup>237</sup>Np agreed to within nearly 5% with those of the calculations. This phenomenon, in which the measurements and the calculations did not agree, may have resulted from the input data of the library for the ORIGEN-2 code. However, the exact reason for this was not identified in this study.

#### 4. CONCLUSION

Determination of the transuranic elements in spent nuclear fuel samples was successfully performed using tracers or a spike, respectively, depending on the elements. The application of the spike addition method for <sup>237</sup>Np in spent fuel samples was established by alpha and gamma spectrometry using <sup>239</sup>Np as a spike.

A comparison between the measurements and the calculations for high burnup PWR spent fuel samples (40~60GWD/MTU) showed that the Pu isotopes and <sup>237</sup>Np agreed to within 10% while <sup>241</sup>Am, <sup>244</sup>Cm and <sup>242</sup>Cm showed higher values of as much as 35% compared to the calculations.

In the future, more data on the transuranic elements of spent fuel samples will be needed for fuel characterizations and code verifications.

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