Burnup Measurement of Irradiated Uranium Dioxide Fuel by Chemical Methods

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화학적 방법에 의한 핵연료의 연소도 측정

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Abstract

Destructive methods are used for the burnup determination of an irradiated PWR fuel. One of the methods includes U, Pu, Nd-148 and Nd-(145+146) determination by an isotope dilution mass spectrometry using triple spikes (U-233, Pu-242 and Nd-150). The method involves two sequential ion exchange resin separation procedures. Pu is eluted from the first anion exchange resin column (Dowex AG 1 × 8) with 12 M HCl- 0.1 M HI mixed solution, followed by U elution with 0.1 M HCl. Nd is isolated from other fission products on the second anion exchange resin column (Dowex AG 1 × 4) with a nitric acid-methanol eluent. Each fraction is analysed by thermal ionization mass spectrometry. The difference between Nd-148 and Nd-(145+146) method is found with an average 2.07%. The results are compared with those by the heavy element method using U and Pu isotopes and by the destructive γ-spectrometric measurement of Cs-137. The dependences of isotope composition of U and Pu on burn-up, and correlation between those isotopes are illustrated graphically.

요 약

PWR 핵연료의 연소도측정은 삼중스파이크(U-233, Pu-242, Nd-150)를 사용한 동위원소 희석 질량분석법으로 U, PU, Nd-148 및 Nd-(145+146)을 정량하여 수행하였다. 이 방법은 먼저 두개의 연속적 이온교환수지 분리과정을 거친다. Pu는 첫번째 음이온 교환수지 분리관(Dowex AG 1 X 8)으로부터 12 M HCl-0.1 M HI 혼합용액으로 분리하고 이어서 0.1 M HCl로 U을 분리하였다. Nd은 질산-메탄올 용리액으로 두번째 음이온 교환수지분리관(Dowex AG 1 X 4) 상에서 분리하였다. 각 부분을 열이온화질량분석법으로 각각의 동위원소비를 측정하였다. Nd-148과 Nd-(145+146) 방법 사이의 차이는 평균 2.07%로 나타났

다. 이 결과를 U과 Pu 동위원소를 이용한 무거운 원소방법 및 Cs-137의 파괴 감마분광측정
법과 비교하였다. 연소도에 대한 U과 Pu의 동위원소 조성의존도와 동위원소사이의 상관관계
를 그래프로서 설명하였다.

I. Introduction

One of the important parameters required for studies of a nuclear fuel is burnup, which is the number of fission per 100 heavy nuclide atoms (mass≥235) initially present in the fuel. Various methods were developed to measure the burnup both by non-destructive and by destructive techniques.

Non-destructive methods included γ-spectrometry, calorimetric determination, neutron counting, mass loss determination, and reactivity change measurement, however, γ-spectrometry is thought to be the most widely applicable method, so far[1-4]. Yet the non-destructive γ-spectrometric method has some limitation in its precision and the accuracy, and required appropriate corrections, the method is used effectively to determine a relative burnup distribution of the fuel. Destructive method, which is based on the determination of specific nuclides by chemical anlaysis after appropriate separation procedures, is widely used as a reference method to measure a burnup of irradiated fuel[5,6]. Destructive method can be classified into two fields according to the elements concerned. One is based on the determination of heavy element depletion before and after irradiation. This method is said to be very accurate in principle, however, to obtain a reliable result, it is required to get an identical sample before and after irradiation. Moreover, accurate reactor parameters such as capture-to-fission cross-section ratio and neutron spectra information must be provided for the calculation of the burnup[5,7-10].

Another destructive method is to determine a burnup monitor element selected from fission products in the irradiated fuel. Ideally, to be used as a burnup monitor, a fission product should:

1) have the same fission yield for all fissioning isotopes of interest in the fuel,
2) not be present in the fuel as an impurity,
3) not be formed during irradiation by any other process,
4) have a small absorption cross-section for neutron capture, have precursors with short half-life and/or small absorption cross-section negligible, have no gaseous precursors be stable or have a long half-life and not migrate through or not be lost from the fuel,
5) be easily separated chemically from the irradiated fuel, and
6) be readily determined by an accurate analysis procedure.

Nd isotope meets all these requirements, but for U and U-Pu fuels, Nd-148 meets most of them[6,11-14]. But a serious drawback with Nd-148 is its reported susceptibility to a Nd-147 neutron capture effect. Maeck et al. postulated an unknown thermal neutron capture cross-section for Nd-147 which would cause increasing amounts of Nd-148 with increasing neutron flux. Therefore the reported number of fissions exceeded the actual number of fissions because of excess Nd-148 being produced from neutron capture on Nd-147. Thus the ASTM Nd-148 procedure includes a correction for Nd-148 formed from Nd-147 due to the neutron flux and fluence[6,15,16].

An approach is to use another monitor such as the sum of Nd-145 and Nd-146 because it appears invariant with neutron flux and fluence. While Nd-145 has a significant capture cross-

section, the Nd-145 production cross-section from Ce-144 and Nd-144 is small and approximately equivalent to the burn-out cross-section on Nd-146.

γ-spectrometry is also applicable in the destructive measurement of burnup[7,17-20]. Among γ-emitters such as Cs-137, Cs-134, Ce-144, Zr-95, Ru-103, Ru-106, Ba-140 and Eu-154, Cs-137 can be used as a monitor.

The aim of this work is to determine the total burnup by different destructive methods on the same sample from an irradiated fuel and to compare the results for the validity of the methods available in the KAERI. The burnup measurement is carried out by three methods as follows:

1) U and Pu method based on the determination of the elements' isotope ratio,

2) Nd-148 and Nd-(145 + 146) method based on the determination of Nd-148, Nd-145 and Nd-146, and

3) γ-spectrometric method based on the determination of Cs-137 activity.

II. Experimental

1. Standard materials

All spikes were obtained from the Oak Ridge National Laboratories and their isotopic compositions were described in the certificate as Table 1. The spike solutions were prepared by dissolving the materials in d-HNO₃ (1 + 1) with 0.01M HF. Final concentrations of the spike solution were 1.1045 mg U/ml for U-233, 3.6748 μg Pu/ml for Pu-242, and 1.7939 μg Nd/ml for Nd-150, respectively.

NBS 950b U₃O₈ powder (National Institute of Standards and Technology, Gaithersburg, MD. 20899) was used as a reference standard material for U. Pu was supplied from Amersham International Ltd. (Amersham, UK) and Nd standard

solution was obtained from Spex Industries Inc. (Santa Clara, CA. 95051, U.S.A.).

The solutions were stored in a tightly sealed container until needed. All other chemicals were of reagent grade purity. Ion exchange resin was purchased from Bio Rad Chemical Div. (Richmond, CA. 94804).

Table 1. Isotopic Composition of Spikes from ORNL

Spike	Isotopic Composition (Atom %)	
U-233	U-233	99.540
	U-234	0.184
	U-235	0.062
	U-236	0.013
	U-238	0.203
Pu-242	Pu-238	0.004
	Pu-239	0.005
	Pu-240	0.022
	Pu-241	0.035
	Pu-242	99.930
Nd-150	Nd-142	0.77
	Nd-143	0.39
	Nd-144	0.88
	Nd-145	0.34
	Nd-146	0.84
	Nd-148	0.66
	Nd-150	96.13

2. Instruments

Mass spectrometric measurement of the isotopes was performed with TSN-206SA (CAMECA, Courbevoie, France) equipped with 90° sector magnetic analyzer, with a thermoionization source, an electron multiplier detector, and with Hewlett Packard HP 9825 data acquisition and processing system.

γ-spectrometric measurements of Cs-137 were

carried out with HPGe coaxial detector (CANBERRA) connected with a multichannel analyzer (8000 channel) having FWHM of 2.3 KeV at 1332 KeV of Co-60.

3. Fuel dissolution and sample preparation

Exactly weighed portion of a fuel sample was dissolved in d-HNO$_3$ (1 + 1) under reflux for more than 12 hours in a 15 cm lead shielded hot cell. After dissolution was completed, the Zircaloy sheath was removed, washed with distilled water, dried, and weighed to obtain the exact weight of the fuel dissolved.

Small aliquot of the fuel solution was diluted with d-HNO$_3$ (1 + 1) by weight to contain about 100 to 400 ng of Nd per gram-solution with the aid of ORIGEN calculation for the estimation of nuclides content in the nuclear fuel[21]. This solution was divided into three portions and a portion was transferred to a vial for γ-spectrometric measurement of Cs-137.

Two portions were subjected to determine U, Pu and Nd isotopes with and without spike addition followed by two sequential ion exchange resin separation procedures described below. The spikes were blended to yield the proper concentration ratio fo each nuclide (i.e., U-238/U-233, Pu-239/Pu-242 and Nd-148/Nd-150) in the range of 1 to 2. The solution was evaporated to dryness several times to assure complete U, Pu and Nd isotope exchange. The dried residue was finally dissolved in 12 M HCl solution. Preparation and quantification of the spike used were described elsewhere[5,6].

4. Separation procedures

Chemical separation was carried out for both the unspiked and the spiked sample solutions in exactly the same experimental conditions in a glove box without heavy shieldings. All chemical treatments and separation procedures were shown in Fig. 1. Pu was eluted from the first column with 12 M HCl-0.1 M HI mixture followed by U with 0.1 M HCl. Nd fraction was isolated from other fission products on the second column with methanol-HNO$_3$ medium, 0.04 M HNO$_3$-99.6% HNO$_3$ (1:9) eluent in the chromatographic condition established.

The Nd portion was subjected to mass spectrometric measurement without further purification. Fractions collected as above procedure were dried in a 5 ml vial, dissolved in 2-3 drops of 1 M HNO$_3$, and reserved for mass spectrometry.
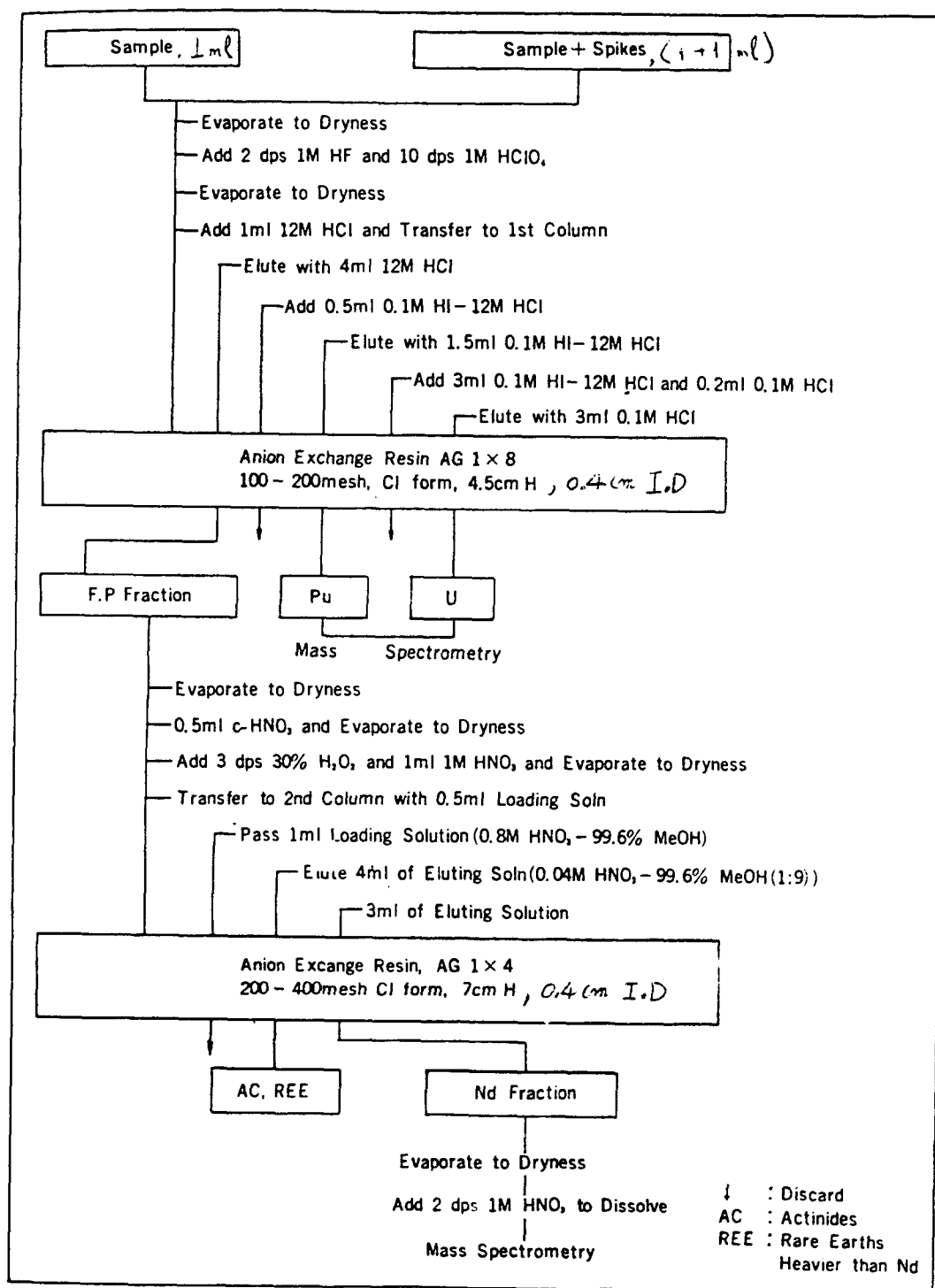
Fig.1.   U, Pu and Nd Separation Procedure.

5. Mass spectrometric measurements and calculation of burnup.

Isotopic compositions of U, Pu, and Nd were measured by the thermoionization mass spectrometer. Sample solutions containing each element were deposited on a triple rhenium filament served as an ion source. Corrections were made on the mass discrimination bias for all elements of interest.

Burnup calculation was made according to ASTM E244-80 and E321-79 from the data obtained from the measurements.

— U and Pu method

$$Ft = F5 + F9 + F1 + F8$$

Ft: Total heavy element atom percent fission
F5, F9, F1, F8: Heavy element atom percent fission from of U-235, Pu-239, Pu-241, and U-238

— Nd-148 and Nd-(145+146) method

$$Ft = [F'/(U' + Pu' + F')] \times 100$$

F' : The number of fission per sample
U' : The total U atoms per sample
Pu': The total Pu atoms per sample

— Cs-137 method

$$Ft = [F/(U + F)] \times 100$$

Ft: U atom percent fission
F : fissions per milliliter of solution
U: number of U atoms per milliliter of solution

III. Results and Discussions

1. Separation procedures

A major advantage in isotope dilution mass spectrometry(IDMS) is that quantitative recovery of the elements concerned is not required. A yield and a purity which give enough material for mass spectrometry are sufficient. Prior to load on the filament, small amount of 1 M $HClO_4$ was used to assure all the Pu in Pu(VI) state because Pu(VI) is more strongly adsorbed on an anion exchange resin as negatively charged chloride complex forms. The Am was not appeared in the Pu and U portions and eluted from the first column (Fig. 1) with the other fission products. Elution of the Pu with 12 M HCl-0.1 M HI and the U with 0.1 M HCl were performed satisfactorily, and no further purification was needed.

The effluent containing fission products and actinides other than U and Pu from the first column was evaporated with HNO_3 to convert the elements into nitrate salts. H_2O_2 was used to reduce the Ce to Ce^{3+} because Ce^{4+} produced by the $HClO_4$ fuming was not completely separated from the Nd fraction in the second column. Alcoholic eluent, 0.04 M HNO_3-99.6% MeOH (1:9) was found satisfactory to obtain a pure Nd fraction separated from the Ce and the Sm.

This is very important because the isobaric pair (Nd-150, Sm-150) interferes directly with the isotope analysis of Nd to cause errors in burnup results, and Ce-142 disturbs the Nd-142 measurement which is essential to correct probable contamination of a natural Nd. The absence of the interfering isobars from the elements was verified through examining the mass spectrum from the masses 140 to 150. In practice, the contribution of natural Nd was found in between 0.3 to 0.8 atom % of the total Nd measured.

Fig. 2. shows anion exchange chromatogram

of the fuel solution used in this study. Major advantages in this chromatographic separation were the use of single elution agent, needless of additional purification steps in other separation procedure, expecting the possibility of sequential separation, and room temperature operation.
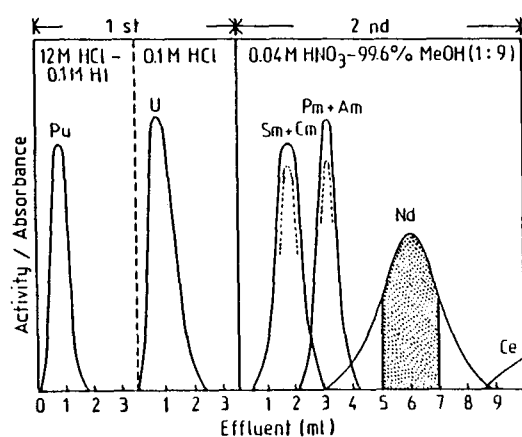

Fig. 2. Anion Exchange Chromatogram with 12 M HCl-0.1 M HI, 0.1 M HCl and Methanolic- HNO₃ Eluent

2. Burnup measurement

Table 2 shows results of the burnup measurements by three methods employed in this study. Burnup data between Nd-148 and Nd-(145 + 146) method showed a good agreement within average relative difference of 2.07%. The results indicate that Nd-(145 + 146) can also be served as a burnup monitor of PWR fuel. The Nd-148 results are consistently higher than those of the corresponding Nd-(145 + 146), and it is probable that a systematic difference between two methods exists. The Nd-148 results not corrected for the Nd-147 neutron capture effect were biased highly up to 3.5% relatively. The results from U and Pu methods were in average difference of 5.54% compared with the Nd-148 method, but major difference was in the case of low burnup.

The values derived from the Cs-137 were generally higher than those from the other methods and were in average difference 7.9%

Table 2. Burn-up in Atom Percent Measured by Different Methods

Sample	Atom % fission			
	Nd-148	Nd-(145 + 146)	U-Pu	Cs-137
P-1-1	3.096	3.081	3.132	—
P-2-1	2.886	2.881	2.937	—
P-2-2	3.675	3.589	3.593	—
P-2-3	3.681	3.637	3.561	—
P-3-1	1.470	1.461	1.702	—
P-3-2	3.753	3.540	3.599	—
P-3-3	3.664	3.627	3.547	—
P-4-1	2.356	2.340	2.421	2.474
P-4-2	3.032	2.925	2.971	3.194
P-4-3	3.128	3.048	3.007	3.364
P-5-1	1.411	1.474	1.753	1.587
P-5-3	3.738	3.673	3.632	4.097
P-5-6	3.761	3.669	3.581	4.040

— MWD/MTU = (9600 ± 300) × Atom % Fission

compared with the Nd-148 method. Larger discrepancies of the two methods were possibly come from the uncertain reactor opeation parameters such as neutron flux and fluence, irradiation and cooling time, etc.

3. Isotope Correlation

A consistency check of the most important quantities determined by post-irradiation analyses has been attempted by means of the isotope correlation technique. Isotope correlations are of great importance for the solution of some analytical and technological problems of the nuclear fuel cycle as well as safeguards problems. The correlation techniques can also be used for the determination of different nuclide concentration and parameters of an irradiated fuel.

In Fig. 3., the Pu/U mass ratio in the irradiated fuel is plotted against the total burnup obtained by the Nd-148 method and those calculated from ORIGEN code. The dependence of U isotope composition (U-235, U-236, U-238) on burnup is demonstrated in Fig. 4. The same dependence for Pu siotopes is shown in Fig. 5. The dependence for U is characterized by a decrease of U-235 and by an increase of U-236 and U-238 with increasing burnup. Similarly, the dependences of Pu composition on burnup is characterized by a decrease of Pu-239 percent content and an increase of Pu-240, Pu-241, and Pu-242 content.

The correlation can be also expressed in the form of isotope ratios, U-235/U-238 against U-236/U-238, U-236/U-238 against the depletion of U-235 or the burnup, U-235/U-238 against the burnup, and Pu-240/Pu-239 against U-235/U-238. All the results showed in the figures were consistent with the values calculated from ORIGEN code within a reasonable range of error.
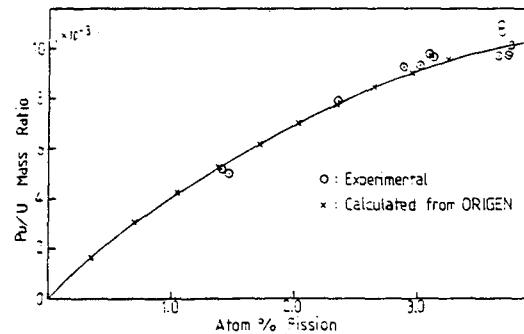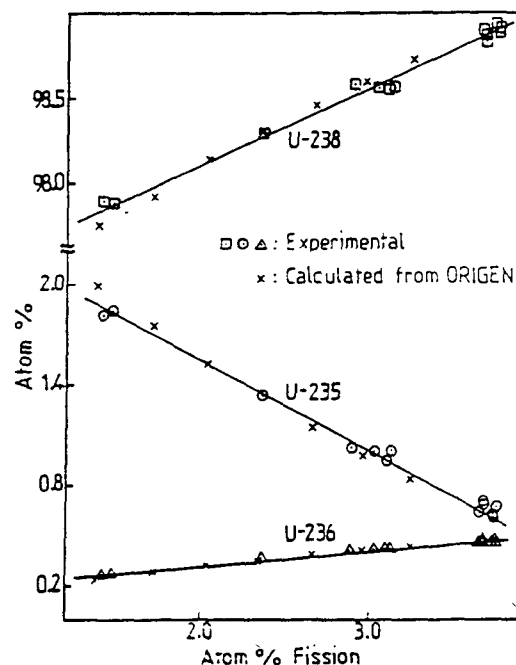

Fig. 3. Correlation between Pu/U Mass Ratio and Burn-up
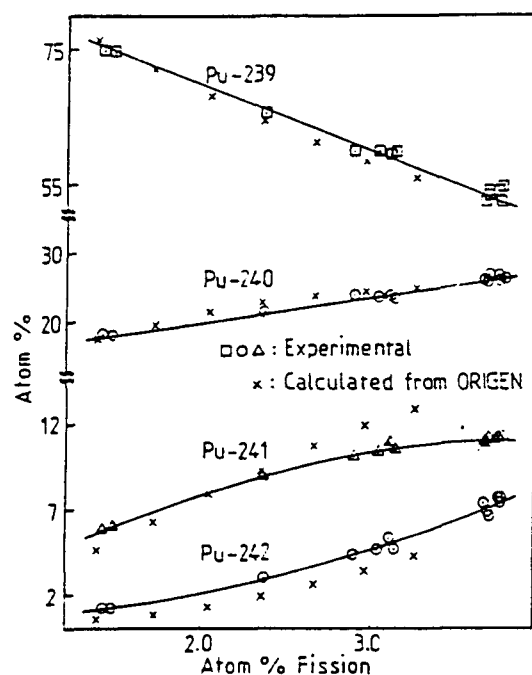

Fig. 4. The Dependence of U Isotope on Burn-up

Fig. 5. The Dependence of Pu Isotope on Burn-up

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