

DISSOLUTION AND BURNUP DETERMINATION OF IRRADIATED U-Zr ALLOY NUCLEAR FUEL BY CHEMICAL METHODS

JUNG SUK KIM¹, YOUNG SHIN JEON, SOON DAL PARK, BYUNG CHUL SONG, SUN HO HAN and JONG GOO KIM

Korea Atomic Energy Research Institute

150 Dekjin-dong, Yuseong-gu, Daejeon, 305-353, Korea

¹Corresponding author. E-mail : njskim1@kaeri.re.kr

Received January 12, 2005

Accepted for Publication February 4, 2006

Destructive methods were used for the burnup determination of U-Zr alloy nuclear fuel irradiated in the High-flux Advanced Neutron Application Reactor (HANARO) at KAERI. The dissolution rate of unirradiated U-Zr alloy fuel in HNO₃/HF mixtures was investigated for the experimental conditions of a different temperature, and initial concentrations of HF and HNO₃. The irradiated U-Zr alloy fuel specimen was dissolved in a mixed acid condition of 3 M HNO₃ and 1 M HF at 90°C for 8 hours under reflux. The total burnup was determined from measurement of the Nd isotope burnup monitors. The method includes U, Pu, ¹⁴⁸Nd, ¹⁴⁵Nd+¹⁴⁶Nd, ¹⁴⁴Nd+¹⁴³Nd and total Nd isotopes determination by the isotope dilution mass spectrometric method (IDMS) using triple spikes (²³³U, ²⁴²Pu and ¹⁵⁰Nd). The effective fission yield was calculated from the weighted fission yields averaged over the irradiation period. The results are compared with that obtained by the destructive γ -spectrometric measurement of the ¹³⁷Cs monitor.

KEYWORDS : Burnup Measurement, U-Zr Alloy Fuel, Nd Isotope Monitor, IDMS

1. INTRODUCTION

One of the important parameters required for the study of a nuclear fuel is its burnup, which is the number of fissions per 100 heavy nuclide atoms (mass ≥ 232) initially present in the fuel. Various methods have been developed to measure burnup both by non-destructive and destructive techniques. Destructive methods, which are based on the determination of specific nuclides by a chemical analysis after appropriate separation of the heavy elements and a monitoring fission product, are widely used as a reference method to measure the burnup of spent fuel [1-3]. The use of the fission product ¹⁴⁸Nd as a burnup monitor for nuclear fuel is generally accepted as a standard method since the issue of the ASTM method E 321-69 [4].

The isotope ¹⁴⁸Nd was selected mainly because its fission yield is independent of the fissioning actinide, and because of its low thermal neutron capture cross-section. However, a serious drawback of ¹⁴⁸Nd burnup monitor is its reported susceptibility to a ¹⁴⁷Nd neutron capture effect. Maeck [5] postulated a large thermal neutron capture cross-section for ¹⁴⁷Nd which would cause increasing amounts of ¹⁴⁸Nd with increasing neutron flux. Therefore, the repor-

ted number of fissions exceeded the actual number of fissions because of excess ¹⁴⁸Nd being produced from the neutron capture on ¹⁴⁷Nd. The isotope ¹⁴²Nd, meanwhile, is used to monitor and correct possible contamination of the fission product with natural Nd during chemical separation. Another approach is to use a different monitor such as ¹⁴⁵Nd+¹⁴⁶Nd because the sum of ¹⁴⁵Nd and ¹⁴⁶Nd appears to be invariant with neutron flux and fluence [2,3,6]. While ¹⁴⁵Nd has a significant capture cross-section, the ¹⁴⁵Nd production cross-section from ¹⁴⁴Ce and ¹⁴⁴Nd is small and approximately equivalent to the burn-out cross-section for ¹⁴⁶Nd.

KAERI (Korea Atomic Energy Research Institute) has been developing SMART (System-integrated Modular Advanced Reactor), a 330 MWt integrated reactor. U-Zr alloy fuel with an enrichment of 8.1 w/o, which consists of 37.2 wt.% U-62.8 wt.% Zr, is used for the SMART design. The irradiated U-Zr alloy fuel contains large amounts of fission products and Zr from the fuel matrix. It has been reported that the U-Zr alloy fuel can be dissolved by applying a mixture of HF and HNO₃, NH₄NO₃ and H₂O₂, HF and KF, ethyl acetate-bromine, and HCl at 300-400°C [7]. The corrosion rate of Zr and Zr-based alloys in HNO₃ is

very small because a very resistive layer of zirconium oxide prohibits direct attack of the metal by an aggressive solution [8]. The retardation of the reaction is due to the very low dissolution rate of the oxide. This rate, however, can be dramatically enhanced by adding HF to the solution. The rate increases with increasing acid concentration.

The aim of the present work is to determine the total burnup by using various Nd monitors for the same sample from an irradiated U-Zr alloy fuel and to compare the results for the validity of the methods. In this paper, experiments are described for the dissolution of unirradiated fuel samples to establish the optimum conditions for complete dissolution and dissolution of the irradiated fuel sample for burnup measurement, as well as for determination of the isotope compositions of U, Pu and the fission product Nd after their separation by ion exchange separation techniques from the fuel sample, determination of the elements in the irradiated fuel by the isotope dilution mass spectrometric method using ^{233}U , ^{242}Pu and ^{150}Nd as spikes, and determination of the total burnup by another method using a ^{137}Cs monitor.

Table 1. Isotopic Compositions of Certified Spikes from ORNL

Spike	Isotope	Atom %
^{233}U	U-233	99.470
	U-234	0.166
	U-235	0.064
	U-236	0.015
	U-238	0.282
^{242}Pu	Pu-238	0.0009
	Pu-239	0.0826
	Pu-240	0.0108
	Pu-241	0.0009
	Pu-242	99.9033
	Pu-244	0.0015
^{150}Nd	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. EXPERIMENTAL

2.1 Chemicals and Instruments

Certified ^{233}U (99.470 atom %) and ^{150}Nd (96.13 atom %) spikes were obtained from Oak Ridge National Laboratory (ORNL). The spike solutions were prepared by dissolving the oxides in HNO_3 (1+1)-0.01 M HF. NBL CRM 129 U_3O_8 powder (New Brunswick Laboratory) and a U standard solution (Spex Industries Inc.) was used as a reference standard material for the U. Neodymium standard solutions were obtained from AccuTrace and Spex Industries Inc.. Certified ^{242}Pu spike solution (99.9033 atom %, IRMM-044) was obtained from the Institute for Reference Materials and Measurements (Table 1). The U-Zr alloy fuel in this work was irradiated at neutron flux of $3.0 \text{ E} + 14 \text{ n/cm}^2 \cdot \text{sec}$ in the Hanaro reactor in KAERI for 96 days (46.0 EFPD), and then cooled for two years for the post-irradiation analyses. The isotopic compositions of U, Pu and Nd separated from an irradiated U-Zr fuel sample were determined using a Finnigan MAT 262 mass spectrometer. Gamma-spectrometric measurements of ^{137}Cs were carried out with a HPGE coaxial detector (EG & G ORTEC) connected to a multi-channel analyzer. Determination of the U in the irradiated fuel sample for the burnup measurement (^{137}Cs monitor method) was carried out with an Ion Chromatography Inductively Coupled Plasma Mass Spectrometer (IC-ICP-MS, Dionex & Finnigan MAT) system with a glove box.

2.2 Dissolution Rate Measurement of Unirradiated U-Zr Fuel

The unirradiated U-Zr alloy samples (0.644 g) were vertically suspended in a 30 mL Teflon bottle, which was kept at a preset temperature in a water bath. 10 mL HNO_3 /HF mixtures of different concentrations were added, and the samples were dipped for 10 minutes. The samples were removed and immediately rinsed with deionized water. After drying and weighing, the samples were put back into the same solution. The weight loss Δm (in g/cm^2) was determined for all the experiments.

2.3 Irradiated U-Zr Fuel Dissolution and Sample Preparation

Basic processes in the PIE analytical laboratory for the burnup determination are shown in Fig. 1. An irradiated U-Zr fuel sample (0.106 g) having been precisely weighed was placed into a 100 mL dissolution flask of the dissolution apparatus with a separatory funnel. 15 mL of 3 M HNO_3 -1M HF without a catalyst was then added dropwise, while applying water cooling. The fuel sample was refluxed for more than 8 hours. The dissolved fuel solution was weighed and an aliquot was diluted with HNO_3 (1+1) to give a ^{146}Nd concentration of about 200 ng per mL solution with the aid of an ORIGEN [9] calculation for estimation of the nuclides content in the irradiated nuclear fuel. An aliquot of the diluted fuel solution was placed in a capped

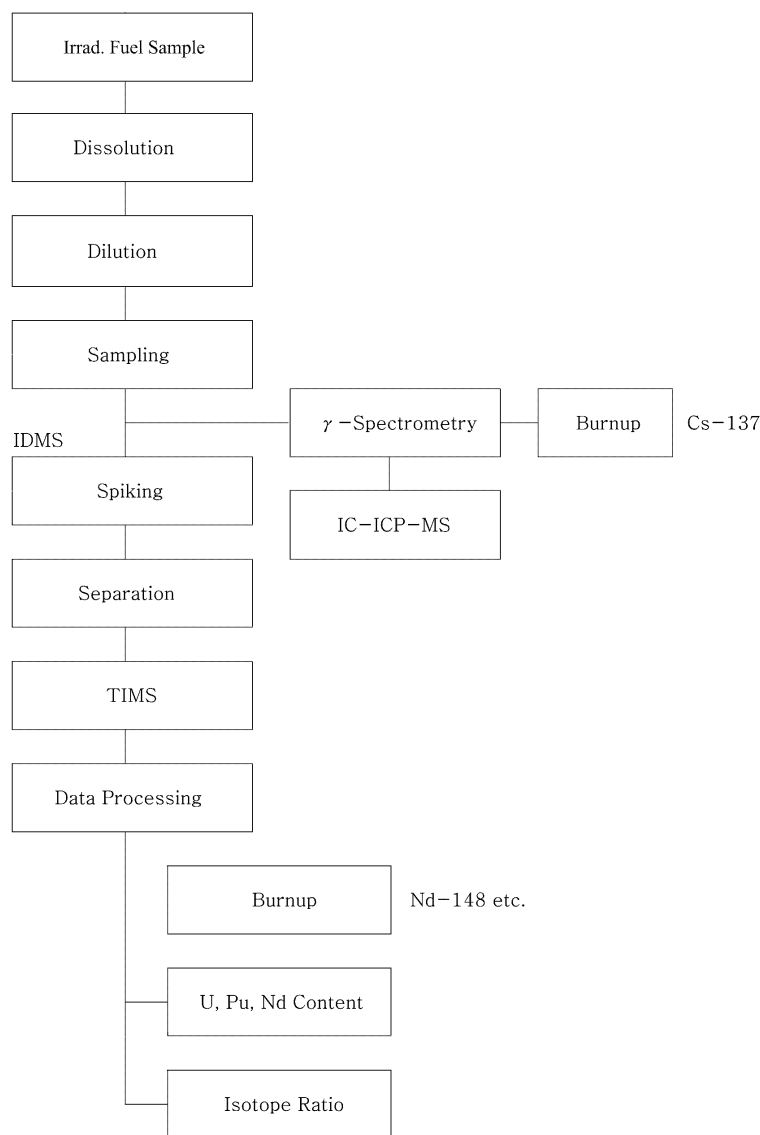


Fig. 1. Basic Processes in the PIE Analytical Laboratory

vial and transferred from the shielded facility into a glove box.

2.4 Separation and Mass Spectrometric Measurement

Chemical separation was carried out for both the unspiked and the spiked sample solutions in the same experimental conditions in a glove box without heavy shieldings. Two portions were subjected to determination of the U, Pu and Nd isotopes in the samples with and without a spike addition followed by the two sequential anion exchange separation procedures detailed in our previous work [2,3]. Isotopic compositions of U, Pu and Nd

in each fraction that had been isolated and concentrated were measured using a thermoionization mass spectrometer (TIMS). Each sample solution of U, Pu and Nd in the range of μg to ng were loaded onto a triple rhenium filament and then measured. The mass discrimination bias and the contribution of natural Nd for all the Nd isotopes measured was corrected [1,10].

2.5 Calculation of the ^{235}U Burnup and Burnup Parameters

^{235}U burnup, the F_5 (fractional burnup from fission of ^{235}U) value in atom % fission, was calculated by the mass spectrometric method according to equation (1) [11,12] :

$$\text{Atom \% fission } (F_5) = N^{08} [(R^{05}/8 - R5/8) - (R6/8 - R^{06}/8)] \quad (1)$$

where N^{08} : atom % abundance of ^{238}U in the pre-irradiated fuel sample
 $R^{05}/8$: atom ratio of ^{235}U to ^{238}U in the pre-irradiated fuel sample
 $R^{06}/8$: atom ratio of ^{236}U to ^{238}U in the pre-irradiated fuel sample
 $R5/8$: atom ratio of ^{235}U to ^{238}U in the post-irradiated fuel sample
 $R6/8$: atom ratio of ^{236}U to ^{238}U in the post-irradiated fuel sample

Some burnup parameters were calculated for correlation studies with U, Pu and Nd isotope ratios.

Symbol	Definition	Reference
D_5	Depletion $[W_s^0/(W_s^0 - W_s)]$ of ^{235}U in weight	[13]
α_5	Capture-to-fission ratio of ^{235}U	[14]
Pu/U	Plutonium-to-uranium ratio in weight	[13]
$N_{F235}/N_{F239}/N_{F241}$	Ratio of fission contributions of ^{235}U , ^{239}Pu and ^{241}Pu	[15]

2.6 Calculation of the Effective Fission Yield and Total Burnup

Total burnup (F_t) value in atom % fission was calculated using different Nd isotope monitors according to equation (2) [1] :

$$\text{Atom \% fission } (F_t) = \frac{N/Y}{N/Y + N(U) + N(\text{Pu})} \times 100 \quad (2)$$

where N : number of atoms of the monitor Nd isotope in the irradiated fuel solution,

Y : effective fission yield of the monitor Nd isotope from the fissile elements,
 $N(\text{U}), N(\text{Pu})$: number of U and Pu atoms in the irradiated fuel solution, respectively

Y value is provided by the average weighted fission yield calculated according to equations (3) and (4) [16] :

$$Y = f \cdot Y_{(x)W}(\text{thermal}) + (1-f) \cdot Y_{(x)W}(\text{fast}) \quad (3)$$

where f : fraction of the thermal fissions
 $Y_{(x)W}(\text{thermal})$: weighted average thermal fission yield for isotope x
 $Y_{(x)W}(\text{fast})$: weighted average fast fission yield for isotope x

$$Y_{(x)W} = 1/2 [(\sum_i N_i \sigma_i \gamma_i / \sum_i N_i \sigma_i)_B + \sum_i N_i \sigma_i \gamma_i / \sum_i N_i \sigma_i]_E \quad (4)$$

where $Y_{(x)W}$: weighted average fission yield for isotope x
 γ_i : fission yield for fissionable isotope i
 N_i : concentration of fissionable isotope i
 σ_i : fission cross-section for fissionable isotope i
 B : at the beginning of irradiation
 E : at the end of irradiation

Total burnup (F_t) value in atom % fission using a ^{137}Cs isotope monitor was calculated according to equation (5) [17].

$$\text{Atom \% fission } [F_t (\text{Cs}-137)] = [F / (U + F)] \times 100 \quad (5)$$

where F : fission per mL of a solution
 U : atoms of uranium per mL of a solution

3. RESULTS AND DISCUSSION

3.1 Dissolution of Unirradiated U-Zr Fuel

We studied the dissolution of a nuclear fuel based on a slice of a rod and a chip of unirradiated U-Zr alloy fuel in a HNO_3 , HF, NH_4F , HCl/HNO_3 mixture, $\text{NH}_4\text{NO}_3/\text{HNO}_3$ mixture, $\text{NH}_4\text{NO}_3/\text{H}_2\text{O}_2$ mixture, and HNO_3/HF mixture without any catalyst, respectively. The experiments showed that the alloy fuel samples can be dissolved completely in the HF/ HNO_3 mixture. The

percent dissolution rate in the HCl/HNO₃ mixture was in a range of 30~70% while the rate in the other acid mixtures was below 3%. As a result, according to the evaluation for the rate of the dissolution, the HNO₃/HF mixture was applied in this experiment for the dissolution of the U-Zr alloy fuel.

The amount of residue (silica) remaining after dissolution of the U-Zr alloys in the HNO₃/HF mixtures was smallest for 3 M HNO₃. For the 15 M HNO₃-1 M HF mixture, the amount of residue after dissolution at 90°C was more than two times that of the 3 M HNO₃-1 M HF mixture, and a large quantity of NO_x was generated in the dissolution. It is known that metallic U is dissolved in HNO₃ of different concentrations and is dissolved sparingly in HF. In contrast, Zr is dissolved in HF with a high dissolution rate [7]. However, HF attacks the dissolution flask, which is made of a Pyrex glass, dissolving the silica. The dissolved silica is remained as a residue in the samples for the chemical separation. The silica is practically insoluble in water or other acids, except HF, in which it readily dissolves, forming SiF₄. If possible, HF must be added in small portions.

In this experiment for the dissolution rate measurement, dissolution of the unirradiated samples was carried out in a Teflon bottle that was kept at a preset temperature in a water bath equipped in a fume hood. When the dissolutions were carried out in bottles kept at 80°C, a large quantity of NO_x gas was released. The dissolution test at 90°C was abbreviated, since a ventilated enclosure or adequate ventilation system to extract the continuously released NO_x gas was required. In this test, the unirradiated fuel samples

were dissolved in different concentrations of HNO₃-HF within 3 to 4 hours at 80°C. However, the dissolver solution of the real irradiated fuel includes insoluble residue occurring from several components. The insolubles consist of metal phases formed in the fuel during irradiation, reprecipitates from the spent fuel solution, crud (radioactive corrosion products) and fine chips of cladding material formed during chopping of the fuel pin, etc. These insolubles will interfere with the determination of burnup by destructive methods, and therefore the dissolution of the real irradiated fuel should be extended for 8 hours or more. The dissolution of U metal or U-Zr metal in reference [7] was carried out with boiling (ex. 110°C under atmospheric pressure). However, it is important to work at the optimum dissolution rate, as in this way the total amounts of U and fission product monitors in the dissolution bottle can be reduced. Dissolution with the dissolver solution being held at near boiling temperature (~90°C) is recommended.

The kinematics of the dissolution of the unirradiated U-Zr fuel in the HNO₃/HF mixtures was investigated for the experimental conditions of a different temperature and initial concentrations of HF and HNO₃. At the beginning of the dissolution a grey precipitate is formed on the surface of the dissolver solution. Electron probe microanalysis (EPMA) showed that the precipitate contained uranic fluoride, such as UF₄ (Fig. 2). This precipitate was completely dissolved with an increase of dissolution time. In all cases the dissolution rate decreased with time; specifically, at the beginning of the experiments, the weight loss curves appeared a steep increase, but later leveled off. Typical

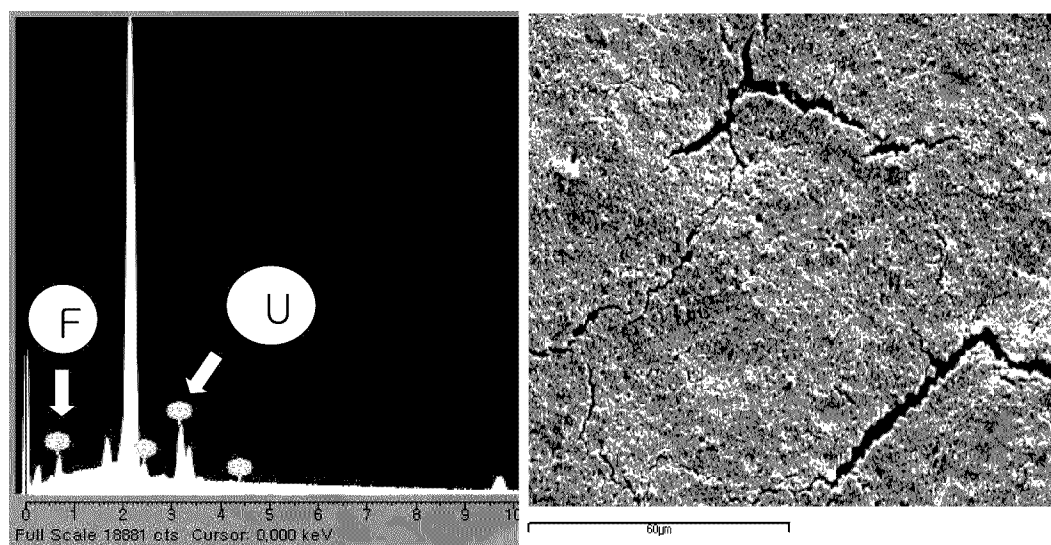


Fig. 2. Scan of the X-ray Spectrum and SEM Image for the Suspended Precipitate Formed at the Beginning of the Dissolution

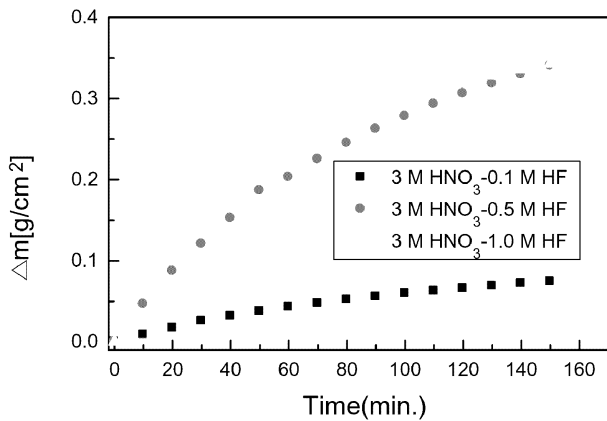


Fig. 3. Weight Loss Curves for the Reactions with the Initial HF Concentrations of 1.0, 0.5 and 0.1 mol/L in 3 M HNO₃ at a Temperature of 30°C

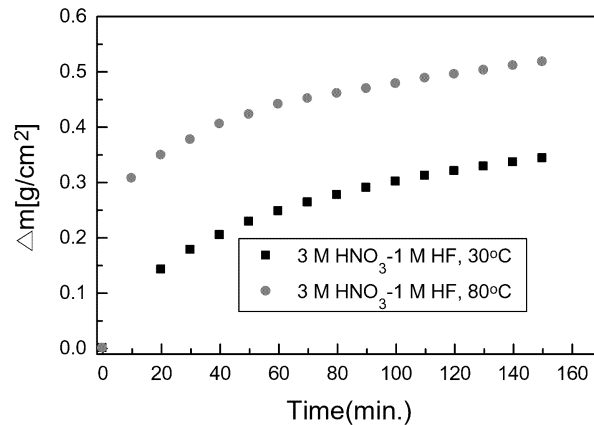


Fig. 4. Weight Loss Curves for the Reactions with the Initial HF Concentration of 1.0 mol/L in 3 M HNO₃ at a Different Temperatures of 30°C and 80°C

examples of the weight loss curves are given in Figs. 3-6.

The dependency of the dissolution rates on the HF concentration in the solutions containing U-Zr alloys is shown in Fig. 3. The overwhelming influence of the HF concentration on the dissolution kinematics is obviously shown. The weight loss rate (0.343) of the 3 M HNO₃-1 M HF at 150 min. in Fig. 3 is similar to that (0.340) for the 3 M HNO₃-0.5 M HF, but the dissolution rate of the former is faster than that of the latter. In this experiment for the dissolution rate measurement, pure U-Zr alloy without cladding (Zr-Nb) was used, whereas the real irradiated U-Zr alloy fuel transferred for dissolution at a hot laboratory includes cladding and Zr produced by fission. That is, the Zr portion in the real irradiated U-Zr fuel is somewhat higher than that of the pure U-Zr alloy used in the preliminary experiments. It is therefore believed that 3 M HNO₃-1 M HF would be effective for complete dissolution of the real irradiated fuel sample.

Fig. 4 shows examples of the dependency of the weight loss curves on the HNO₃/HF mixture at different temperatures. Fig. 5 shows examples of the dependency of the weight loss curve on the HNO₃/HF mixture at different HNO₃ concentrations. The overall weight loss as well as the reaction rate for the dissolution of U-Zr alloys apparently depends on the HNO₃ and HF concentrations, as well as the temperature. Consequently, from the experimental results, the 3 M HNO₃-1 M HF mixture was considered as the optimum dissolvent for complete dissolution of all the irradiated U-Zr alloy fuel, where dissolution continues for 8 hours at 90°C.

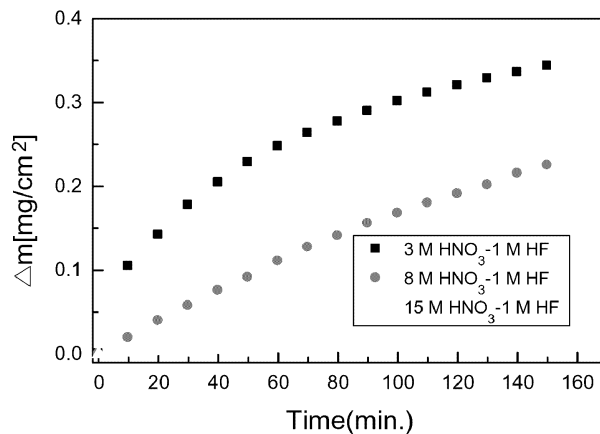


Fig. 5. Weight Loss Curves for the Reactions with the Initial HF Concentration of 1.0 mol/L in 3 M, 8 M and 15 M HNO₃ at a Temperature of 30°C

3.2 Separation and Determination of Isotopic Composition

A series of preliminary experiments on the separation of U, Zr and some fission products was performed using the prepared stock solution. Suitable simulated fission pro-

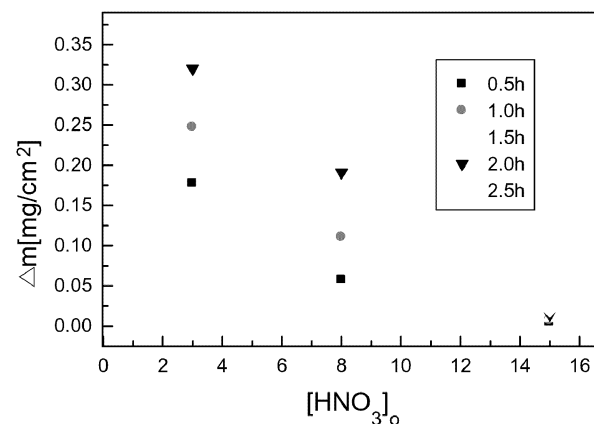


Fig. 6. Dependency of the Weight Loss for the Reactions with the Initial HNO₃ Concentrations of 3, 8 and 15 mol/L in 1 M HF at a Temperature of 30°C

Table 2. Isotopic Compositions of U, Pu and Nd Separated from an Irradiated U-Zr Fuel Sample

U		Pu		Nd	
Isotope	Weight %	Isotope	Weight %	Isotope	Weight %
U-234	0.5251	Pu-238	0.6579	Nd-143	26.8680
U-235	5.7756	Pu-239	89.0831	Nd-144	25.9606
U-236	0.4861	Pu-240	9.2435	Nd-145	19.0043
U-238	93.2132	Pu-241	0.9541	Nd-146	15.6977
		Pu-242	0.0614	Nd-148	8.8865
				Nd-150	3.5829
Total	100.0000	Total	100.0000	Total	100.0000

Table 3. Determination of U, Pu, Nd and their Isotopes in an Irradiated U-Zr Fuel Sample by Isotope Dilution Mass Spectrometry

U		Pu		Nd	
Isotope	Weight (μg)	Isotope	Weight (μg)	Isotope	Weight (μg)
U-234	4.3878	Pu-238	0.0027	Nd-143	0.6769
U-235	48.2603	Pu-239	0.3647	Nd-144	0.6541
U-236	4.0616	Pu-240	0.0378	Nd-145	0.4788
U-238	778.8778	Pu-241	0.0039	Nd-146	0.3955
		Pu-242	0.0003	Nd-148	0.2239
				Nd-150	0.0903
Total	835,5875	Total	0.4094	Total	2.5195

duct elements were added to the solution dissolved with the unirradiated U-Zr alloy and their behavior was studied in separation systems [2,3]. We found that satisfactory chromatographic separation of these elements could be achieved. Therefore, the separation of each element from the irradiated fuel solution was carried out in a glove box with the same separation procedure. The U, Pu and Nd fractions collected from the spiked (^{233}U , ^{242}Pu and ^{150}Nd) and unspiked fuel samples were prepared for mass spectrometric determination. Table 2 shows the isotopic compositions of U, Pu and Nd in an irradiated U-Zr fuel sample measured by TIMS.

For the calibration of the mass spectrometer for the isotope analysis, correction of the mass discrimination is necessary in order to obtain accurate and consistent results. The mass discrimination bias factor is constant for a given method of scanning and detection for a given detector. In this work, all the measured average ratios of Nd were corrected for mass discrimination and the contribution of natural contamination so as to achieve high accuracy for

the burnup measurement [1]. After the mass spectrometric measurement of each portion isolated from the spiked and unspiked sample solutions, the concentrations of U, Pu and Nd in the sample solutions were determined by the isotope dilution method. Table 3 shows the concentrations of U, Pu, Nd and its isotopes in an irradiated U-Zr fuel sample as determined by IDMS. A major advantage of IDMS is that quantitative recovery of the elements concerned is not required.

3.3 Determination of the ^{235}U Fractional Burnup and the Burnup Parameters

Fractional (^{235}U) burnup, F_5 , can be calculated from equation (1) by assuming no loss of ^{238}U or ^{236}U during irradiation. Equation (1) is best applied at high exposure, where more than 10% of ^{235}U is consumed. On the other hand, F_5 from equation (1) is seriously affected by natural U contamination in the irradiated fuel sample. For this reason, precaution must be taken to prevent contamination from U in the chemistry and mass spectrometry operations. The principal merit of equation (1) lies in its independency of the reactor variable, α_5 [effective ratio of $^{235}\text{U}(n,\gamma)$ capture-to-fission cross-sections]. In this work, α_5 was calculated from equation (7) with atom ratios and the number of atoms was determined by IDMS[14].

$$\alpha_5 = (R - R^0) A_5 / (P/Y) = \text{captures} / \text{fissions} \quad (7)$$

where R : atom ratio of $^{236}\text{U} / ^{235}\text{U}$ in the post-irradiated fuel sample

R^0 : atom ratio of $^{236}\text{U} / ^{235}\text{U}$ in the pre-irradiated fuel sample

A_5 : number of ^{235}U atoms in the post-irradiated fuel sample

P : number of atoms of the fission product monitor (^{148}Nd)

Y : fission yield for P

Table 4 shows the F_5 value calculated according to equation (1) together with the α_5 and D_5 values, and the ratio of the fission contributions of ^{235}U , ^{239}Pu and ^{241}Pu . The depletion of ^{235}U (D_5 , the difference between the initial and final ^{235}U content) is expressed by $W_5^0 / (W_5^0 - W_5)$.

In order to check the consistency of the post-irradiation analysis results, the correlations between the parameters of irradiated nuclear fuels and burnup have been studied [2]. These correlations can be used to identify reactor fuels and to estimate the burnup and Pu production. The parameters in Table 4, which are calculated with the isotope compositions and concentrations of U, Pu and Nd measured experimentally, can be used for these correlation studies, e.g. Pu/U vs. total burnup, α_5 vs. $^{235}\text{U}/^{238}\text{U}$, D_5 vs. $^{236}\text{U}/^{238}\text{U}$ and F_5 vs. $^{235}\text{U}/^{238}\text{U}$. To express the dependence between individual isotopes, many experimental data on the basis of the analysis of irradiated U-Zr fuel samples is required.

Table 4. Determination of the Burnup Parameters for an Irradiated U-Zr Fuel Sample

F_3^*	D_3	α	Pu/U	$N_{F235}/N_{F239}/N_{F241}^{***}$
1.9513 ± 0.0064	3.5911 ± 0.0059	0.2024 ± 0.0085	$4.90 \pm 0.02 \times 10^4$	98.12/1.86/0.01

$F_3(\text{Atom \% Fission}) = N^*8[R^{95}/8 - R^{145}/8] - (R^{68} - R^{96}/8)$ [7,9].

*** neglected the fast fissions originating in ^{239}U [15].

$N_{F235}/N_{F239} = [1/(1+P)] \cdot (\sigma_{235}/\sigma_{239}) [(N_{235}/N_{239})_E + P(N_{235}/N_{239})_E]$

$N_{F241}/N_{F239} = [1/(1+P)] \cdot (\sigma_{241}/\sigma_{239}) [(N_{241}/N_{239})_E + P(N_{241}/N_{239})_E]$

Table 5. Estimated Effective Fission Yields for an Irradiated U-Zr Fuel Sample

Fission Product	Nd-143	Nd-144	Nd-145	Nd-146	Nd-148	Nd-150
E.F. Y	5.8965	5.4378	3.8925	2.9770	1.6758	0.6624

E.F. Y : Effective Fission Yield

3.4 Determination of the Effective Fission Yield and the Total Burnup

Walker[18] reported that the variance in the ^{148}Nd isotopic abundance is greater than that of $^{145}\text{Nd}+^{146}\text{Nd}$ and even ^{150}Nd , each of which are slightly affected by the neutron capture processes. That is, the calculated number of fissions exceeded the actual number of fissions because of excess ^{148}Nd being produced from capture on ^{147}Nd . The magnitude of this error is a function of the flux and fluence. This is especially significant for constant prolonged high flux irradiations. However, a significant fraction of reactor down time will reduce the magnitude of the capture effect [19]. Another approach is to use a different monitor such as $^{145}\text{Nd}+^{146}\text{Nd}$, because the sum of ^{145}Nd and ^{146}Nd appears to be invariant with neutron flux and fluence. In the thermal reactor spectra, considerable burnout of ^{145}Nd and ^{146}Nd occurs, becoming ^{144}Nd and ^{146}Nd , respectively. Therefore, their fission yields and their abundances in the fission product Nd have to be added. In addition, if short-cooled fuel is examined, a substantial fraction of mass 144 is still present as ^{144}Ce , and the abundance of ^{144}Nd should be corrected accordingly.

In this work, burnup values (in atom % fission) of an irradiated U-Zr fuel sample by various Nd isotope monitors (^{148}Nd , the sum of ^{145}Nd and ^{146}Nd , the sum of ^{145}Nd and ^{144}Nd , and the sum of total Nd isotopes) were calculated according to a procedure in the references [1,3]. The successful application of this technique requires accurate measurement of the fission product monitor and heavy atoms and an accurate value for the effective fission yield. The effective fission yield was calculated from the weighted fission yields averaged over the irradiation period by equations (3) and (4). The concentration of the

Table 6. Total Burnup in Atom % Fission Determined by Chemical Methods for an Irradiated Fuel Sample

Isotope	$F_T(\text{Atom \% Fission})$	Difference
Nd-148(C)	2.1720 ± 0.0195	1.000
Nd-(145+146)	2.2389 ± 0.0202	1.031
Nd-(143+144)	2.0817 ± 0.0187	0.958
Nd-Total	2.1623 ± 0.0195	0.995
Nd-148(NC)*	2.3597 ± 0.0021	1.086
Cs-137	2.4375 ± 0.1414	1.122

Total : 143+144+145+146+148+150

*calculated without correction for excess Nd-148 produced from capture on Nd-147.

fissionable isotopes required for the calculation was determined by IDMS, and the nuclear data was obtained from references [20-22]. Table 5 gives the effective fission yields for all the Nd isotopes calculated from the irradiated U-Zr fuel sample. Table 6 gives the total burnup (atom % fission) measured by Nd isotope monitors, ^{148}Nd , $^{145}\text{Nd}+^{146}\text{Nd}$, $^{145}\text{Nd}+^{144}\text{Nd}$ and total Nd isotopes. From the consideration of the irradiation characteristics and the cooling time for this fuel, the abundance of ^{144}Nd was calculated without correction for ^{144}Ce . The period T (days) and the number of EFPD (effective full power days) of the U-Zr alloy fuel irradiated in the Hanaro reactor was 96 and 46,

respectively (capacity factor ~47%). The number of fissions by the ^{148}Nd monitor, Nd-148(C), was calculated with correction for the excess ^{148}Nd produced from the capture on ^{147}Nd , where the correction factor was calculated on the basis of continuous reactor operation (46.0 EFPD) in a total neutron flux of 3.0×10^{14} n/cm² · sec according to the ASTM E 321-96 [1]. This result is 8.6% lower than the corresponding Nd-148(NC) result, which is calculated without correction for the excess ^{148}Nd produced from the capture on ^{147}Nd . The data obtained using other Nd monitors, $^{142}\text{Nd}+^{146}\text{Nd}$, $^{143}\text{Nd}+^{144}\text{Nd}$ and total Nd isotopes, are in agreement, within 4.2% of that by ^{148}Nd monitor. The use of other Nd isotopes in the determination of the burnup for a nuclear fuel can be used to verify the value obtained for ^{148}Nd . In addition, no additional separation work or mass spectrometric analysis is needed. The agreement of the number of fissions calculated from the isotopes sensitive to fuel composition confirms the fissile isotope content.

For the most accurate burnup analysis, the requester should provide to the measurer an estimate of the neutron flux and irradiation history with respect to the reactor up and down time, from which the appropriate correction factor can be calculated. The reactor cycling time could be important if the downs are frequent and the durations significant when compared to the 11 d half life of ^{147}Nd . The fraction of the down time will reduce the magnitude of the correction. More work is required to accurately determine the ^{147}Nd cross-section and its effect on Nd-148 burnup.

3.5 Comparison of the Total Burnup by Different Method

Table 6 shows the total burnup values determined using ^{137}Cs as a fission monitor (Cs-137 method). The total burnup value by the Cs-137 method was in a range of 12.2% relative difference with the result of Nd-148(C), determined using ^{148}Nd as a fission monitor. The ^{137}Cs method (ASTM E 219-80) is based on the determination of U atom percent fission that occurred in U fuel according to an analysis of the ^{137}Cs to U ratio after irradiation. The advantage of this method is its applicability to dissolved fuel solution without the necessity of chemical separations or elaborate preparation. However, the radioactive fission product, ^{137}Cs , should be completely dissolved with the U to maintain the true ratio of the fission product ^{137}Cs to U. In addition, a quantitative analysis for the U concentration in a sample solution must be carried out separately.

The U determination in this work was carried out by IC-ICP-MS. The accuracy of this method is limited, not only by the experimental error of ^{137}Cs and U, but also by the accuracy with which the fission yield and half life of ^{137}Cs known. A simplified assumption is made that the yield of ^{137}Cs from the thermal fission of ^{235}U is representative of all the fissions occurring in a nuclear fuel. The in-fuel decay corrections necessitate accurate knowledge of the

fuel power history. Other disadvantages of this method are found in the volatility of Cs and its precursors at fuel operating temperature, interference in counting from ^{134}Cs and ^{136}Cs and some uncertainty in physical constants.

4. CONCLUSIONS

Irradiated U-Zr alloy fuel can be dissolved in a mixed acid condition of 3 M HNO₃ and 1 M HF at 90°C for 8 hours under reflux. The use of all the Nd isotopes in the determination of burnup for a nuclear fuel does not require additional work for chemical separation or mass spectrometric analysis. The advantage of considering a whole set of Nd isotopes lies primarily in the confirmation of the value obtained for ^{148}Nd . By the analysis of the other Nd isotopes, it is possible to identify the fission source distribution and quantify the contributions of the different fissile isotopes. The Nd isotope pattern provides information on the real irradiation characteristics, which is necessary for evaluating the fuel performance in the reactor. A comparison between independently determined burnup values provides verification of the validity of the results.

REFERENCES

- [1] American Society for Testing and Materials Standard Method E 321-96, "Atom Percent Fission in Uranium and Plutonium Fuel (Neodymium-148 Method)", 1 (1996).
- [2] J. S. Kim, S. H. Han, M. Y. Suh, K. S. Joe and T. Y. Eom, "Burnup Measurement of Irradiated Uranium Dioxide Fuel by Chemical Methods", *J. Korean Nucl. Soc.* 21(4), 277 (1989).
- [3] J. S. Kim, Y. S. Jeon, K. S. Choi, B. C. Song, S. H. Han and W. H. Kim, "Burnup Measurement of Spent U₃Si/Al Fuel by Chemical Method Using Neodymium Isotope Monitors", *J. Korean Nucl. Soc.* 33(4), 375 (2001).
- [4] American Society for Testing and Materials Standard Method E 321-69, "Atom Percent Fission in Uranium and Plutonium Fuel (Neodymium-148 Method)", 1045 (1969).
- [5] W. J. Maeck, Review Paper No. 5, *IAEA Fission Product Nuclear Data Conference, IAEA-169*, Bologna, Italy, Nov.(1973).
- [6] L. W. Green, N. L. Elliot, F. C. Miller and J. J. Leppinen, "Mass Spectrometric Determination of Burnup of (U,Pu)₂O₇ Fuel Using Nanogram Quantities of Isotopes", *J. Radioanal. & Nucl. Chem. Art.*, 131(2), 299 (1989).
- [7] H. Sorantin, "Determination of Uranium and Plutonium in Nuclear Fuels", *Kernchemie in Einzeldarstellungen*; Vol. 5, Verlag Chemie, Germany (1975).
- [8] Z. Goncalves and H. Munzel, "Dissolution Kinetics of Zircaloy in HNO₃/HF Mixtures", *J. Nucl. Mater.*, 170, 261 (1990).
- [9] S. G. Ro, J. M. Park, D. K. Min, P. I. Choi and H. S. Shin, "Radioisotope Inventories in Spent Fuel from KNU PWR", *KAERI/PIED/note-001/87* (1987).
- [10] L. Koch, "Post-Irradiation Isotopic Analysis of Reactor Fuels", *Analytical Chemistry of Nuclear Fuels, IAEA STI/PUB/337*, 111 (1972).
- [11] American Society for Testing and Materials Standard

- Method E 244-80 (Reapproved 1995)*, "Atom Percent Fission in Uranium and Plutonium Fuel (Mass Spectrometric Method)", 1 (1996).
- [12] J. E. Rein and C. F. Metz, "Advantages and Limitations of Mass Spectrometry for the Measurement of the Isotopic Distributions of Uranium and Plutonium and Application to Nuclear Fuel Burnup", *Analytical Chemistry in Nuclear Fuel Reprocessing, IAEA STI/PUB/337*, 135 (1978).
- [13] J. S. Kim, "Analysis of the Irradiated Nuclear Fuel Using the Heavy Atom and Neodymium Isotope Correlations with Burnup", *J. Korean Nucl. Soc.*, **29**(4), 327 (1997).
- [14] J. E. Rein, "Status of Burnup Measurement Methodology", *Analytical Methods in the Nuclear Fuel Cycle, IAEA-SM-149/40*, 449 (1972).
- [15] P. De Regge, De Huys, R. Boden and C. Ballaux, "Actual Experience in Burnup Determination of Mixed Oxide Fuel", *Proc. of a Technical Committee Meeting Organized by the International Atomic Energy Agency and Held in Karlsruhe, IWGFPT/31*, 23 (1989).
- [16] P. De Regge and R. Boden, "Determination of Neodymium Isotopes as Burnup Indicator of Highly Irradiated (U,Pu)₂O₇ LMFBR Fuel", *J. Radioanal. Chem.*, **35**, 173 (1977).
- [17] *American Society for Testing and Materials Standard Method E 219-80 (Reapproved 1985)*, "Atom Percent Fission in Uranium Fuel(Radiochemical Method)", 57 (1987).
- [18] W. H. Walker, *Atomic Energy of Canada Limited Report AECL-3037*, Part 1 and 2, Chalk River Nuclear Laboratory (1972).
- [19] W. J. Maeck, W. A. Emel, L. L. Dickerson, J. E. Delmore, J. H. Keller, F. A. Duce and R. L. Tromp, "Discrepancies and Comments Regarding ²³⁵U and ²³⁹Pu Thermal Fission Yields and the Use of ¹⁴⁸Nd as a Burnup Monitor", *Idaho Chemical Programs Report ICP-1092*, Idaho National Engineering Laboratory (1976).
- [20] T. R. England and B. F. Rider, "ENDF-349 Evaluation and Compilation of Fission Product Yields 1993", *Los Alamos National Laboratory Report LA-UR-94-3106*, Los Alamos National Laboratory (1994).
- [21] H. Kim, H. R. Kim, K. H. Lee and J. B. Lee, "Design Characteristics and Startup Tests of HANARO", *J. Nucl. Sci. Tech.*, **33**(7), 527 (1996).
- [22] D. R. Lide, *CRC Handbook of Chemistry and Physics*, 74th ed., 11-35, CRC Press, Inc., U.S.A. (1993).