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Correlations between Zirconium Isotopes and Burnup Parameters in PWR Spent Nuclear Fuels

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Abstract

The correlation of isotope composition of Zr with the burnup and some heavy isotopes in PWR uranium dioxide fuel has been investigated. The total and partial(^{235}U) burnup were determined by ^{148}Nd and by U and Pu mass spectrometric method, respectively. After separating Zr from the fuel samples, its isotope composition was measured by mass spectrometry. In addition, the quantities of the U and Pu in the spent fuel were determined by isotope dilution mass spectrometric method using ^{233}U and ^{242}Pu as spikes. The content of some heavy isotopes, ^{235}U, ^{239}Pu and ^{241}Pu, and the Pu contribution to total burnup were expressed by the correlation with Zr isotope ratios, ^{91}Zr/^{96}Zr and ^{93}Zr/^{96}Zr. The correlations by isotope compositions measured were compared with those calculated from ORIGEN2 code.

1. Introduction

The correlations between the fission product isotope ratios and the parameters of spent nuclear fuels have been investigated for the characterization of various spent nuclear fuels. Of many elements, U, Pu and some fission products such as Kr, Xe, Cs, Nd, Eu and Ru

have been mentioned[1-10]in these studies. However, there are a few instances which Zr fission isotopes have been used in nuclear correlation studies[11]. The fuel parameters also includes burnup(total and ^{235}U, partial burnup) and quantities of transuranium elements formed in spent nuclear fuel. The principle of determination of Pu contribution to the total burnup using Zr isotope ratio was based on the use of the difference in fission yield ratios of Zr fission products from two main fissionable nuclides ^{235}U and ^{239}Pu(also ^{241}Pu).

The fission yield ratios of particular isotopes have a constant value for a given fissioning nuclide, as listed in Table 1, where the selected isotope ratios of Zr are presented. However, when the fissions are simultaneously generated in the fuel by the two fissioning nuclides(^{235}U and ^{239}Pu) as is the case with low enrichment fuels, then the resulting fission yield ratios have intermediate values, depending on the contribution of fissions from Pu. By constructing suitable calibration curves based on theoretical calculations and measuring the real Zr fission product ratios, it was possible to determine the Pu contribution to total burnup of the fuel. To do this the following two independent methods have been applied[11]; (1) by measuring isotope ratios of the stable Zr fission products $^{93}Zr/^{96}Zr$ and $^{91}Zr/^{96}Zr$, and (2) by determining the total burnup, F_t, from ^{148}Nd or ^{137}Cs method, and subtracting the partial burnup due to ^{235}U, F_5, determined from ^{235}U depletion method. ^{93}Zr isotope was selected because it does not appear in natural Zr. Natural abundance of two other isotopes ^{96}Zr and ^{91}Zr are the lowest, amounting to 2.80% and 11.2%, respectively.

In this work an attempt has been made to use the isotope ratios of Zr fission products in the isotope correlation studies, both to determine the quantities of U and Pu with their isotopes and the Pu contribution to the total burnup for a PWR fuel from Kori-1.

2. Experimental

2.1. Sample praparation

The fuel in this work was a PWR type with initial enrichment 3.21%. The estimated average burnup of fuel rod was about 4.05 FIMA, and the cooling time was ~9 years. All sample solutions from the fuel specimens were prepared in HNO_3(1+1).

2.2. Chemical separation and mass spectrometry

For burnup determination, U, Pu and Nd, and their spiked portions with ^{233}U, ^{242}Pu and ^{150}Nd were separated from the fuel samples by two step anion exchange chromatography. A detailed description of this procedure is given in Reference 14. The separation of Zr was achieved by anion exchange chromatography on a Dowex 1x8 column. In the first step, the separation was achieved by loading and first eluting the other fission products with 12 M HCl, second eluting Pu with 12 M HCl-0.1 M HI and finally eluting Zr with 5 M HCl. In the second step, further purification of Zr was carried out with anion exchange resin in 5 M HCl in order to get rid of Mo caused isobaric effect. The isotopic composition of U, Pu, Nd and their spiked portions, and Zr was measured with a FINIGAN MAT 262 mass spectrometer equipped with a thermal ionization source.

2.3. Burnup determination and isotope correlations

Total burnup(F_t) value in atom % fission was calculated by the Nd-148 method[12,14,15] and partional burnup(F_5) value in atom % fission was calculated by the mass spectrometry method(^{235}U depletion method)[13-15]. The concentrations of U and Pu in sample solutions were determined by the isotope dilution method. The correlations between the heavy isotopes and the burnup values against $^{91,93,96}Zr$ measured experimentally and also the values calculated from the ORIGEN2 code were plotted.

3. Results and discussion

The isotope composition of Zr separated was shown in Fig. 1. In the spectrum of the Zr fission products a peak ^{90}Zr can be seen. ^{90}Zr is not produced by fission reaction, but is a final decay product in the mass chain in the fission products. Taking into account the

cooling time of the fuel(~9 y), the contribution of ^{90}Zr to the Zr mass spectrum was estimated as being due to the decay of ^{90}Sr and as well the contamination of the fuel sample with natural Zr. However, it is belived that there is no contribution of mass 90 peak by Sr isobar, according to the absence of ^{88}Sr are also formed in the fission processes. The mass 97 and 98 peak is just due to Mo concent in the isolated Zr fraction because no other isotopes of mass 96 and 97 have a sufficiently long half-life to be present in irradiated fuel after decay of a few years. Therefore, Mo would not be present in the Zr fraction and the contribution of ^{96}Mo isobar to the mass 96 peak can be ignored.

From the ratios $^{93}Zr/^{96}Zr$ and $^{91}Zr/^{96}Zr$ determined by experiment and calculation, the calibratiom curves by the following formulas were constructed. Assuming that the total burnup of the fuel is the sum of partial contributions due to U and Pu, $F_u + F_{Pu} = 100$ %, and that the isotope ratio $R_{i/j}$ for the fission isotopes i and j generated from U and Pu different yields(y),

$$R_{i/j} = \frac{F_U\, y^i_U + F_{Pu}\, y^i_{Pu}}{F_U\, y^j_U + F_{Pu}\, y^j_{Pu}}$$

the Pu contribution(F_{Pu}) to the total burnup, it can be expressed by the following equation:

$$F_{Pu} = \frac{(R_{i/j}\, y^j_U - y^i_U) \times 100}{(y^i_{Pu} - y^i_U) - R_{i/j}(y^j_{Pu} - y^j_U)}$$

On the other hand, The Pu contribution could be determined by substracting the partial burnup(F_5) determined from ^{235}U depletion method from the total burnup(F_t) determined from the ^{148}Nd method, $F_{Pu} = F_t - F_5$.

The results obtained by two methods mentioned above are given in Table 2 together with those calculated by ORIGEN2 code. The values of the Pu contribution by the $^{93}Zr/^{96}Zr$ ratio and $F_t - F_5$ from calculated values of ORIGEN2 code are in good agreement, but those of the Pu contribution calculated from experimental results for a fuel sample with similar burnup showed a great difference. It is belived that this disagreement of the experimental results is attributed to the isotope analysis of Zr fraction contaminated with natural Zr.

The correlations of $^{93}Zr/^{96}Zr$ atom ratio on total and partial burnup obtained by the ^{148}Nd method and ^{235}U depletion method respectively are shown in Fig. 2. The dependence of Pu/U

ratio which is determined by IDMS method against $^{93}Zr/^{96}Zr$ atom ratio are shown in Fig. 3. The correlation between ^{239}Pu atom % on $^{93}Zr/^{96}Zr$ atom ratio are also shown in Fig. 4. The dependences of some parameters against the $^{93}Zr/^{96}Zr$ atom ratio showed a good linearity, however, the correlation betweens the isotope ratios on those measured experimentally was different from that of calculation from ORIGEN2 code. It is belived that this disagreement of the expermental results with the calculated one attributed to the analysis of Zr fraction with natural contamination, and it also may be attributed to the partial errors in chemical operations, isotope measurements and uncertainties in nuclear constant.

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Table 1. Fission Yield in the Thermal Neutron Fission of U-235, Pu-239 and Pu-241*

Fission Product	U-235	Pu-239	Pu-241
Zr-91	5.90	2.52	1.82
Zr-92	5.95	3.02	2.23
Zr-93	6.34	3.95	2.90
Zr-94	6.41	4.50	3.33
Zr-96	6.23	5.12	4.33
Zr-93/Zr-96	1.018	0.771	0.670
Zr-91/Zr-96	0.947	0.492	0.420

* from Nucl. Sci. & Eng. 42, 191 (1970)

Table 2. Determination of the Pu Contribution, %

ORIGEN2		Experimental	
isotope ratio $^{93}Zr/^{96}Zr$	burnup difference $F_t - F_5$	isotope ratio $^{93}Zr/^{96}Zr$	burnup difference $F_t - F_5$
44.17	43.20	- 34.61	46.74
38.85	35.92		

F_t : total burnup F_5 : ^{235}U burnup

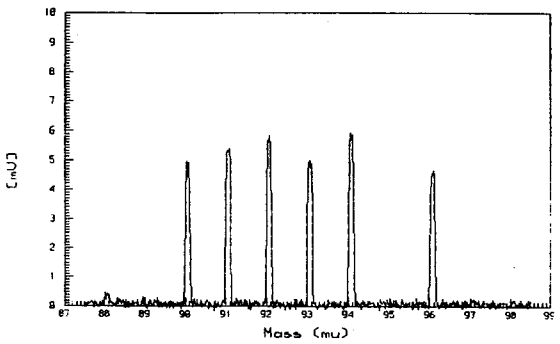

Fig. 1. Mass spectrum of Zr separated from a spent PWR fuel.

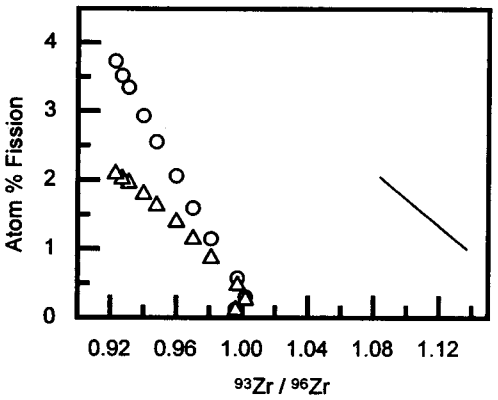

Fig. 2. Correlation between total(F_1), partial burnup(F_5) and $^{93}Zr/^{96}Zr$ atom ratio; O : F_t, Calculated, Δ : F_5, Calculated, ——: F_5, Experimental.

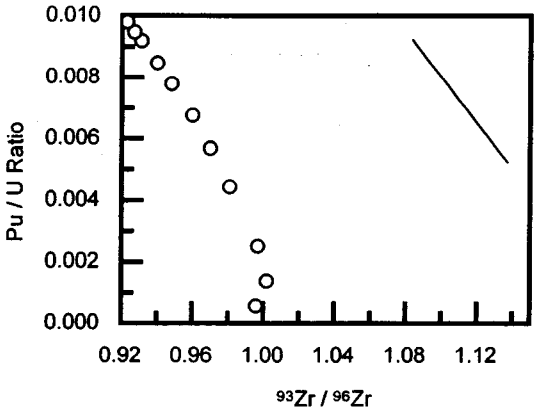

Fig. 3. Correlation between U/Pu ratio and $^{93}Zr/^{96}Zr$ atom ratio; O : Calculated, —— : Experimental.

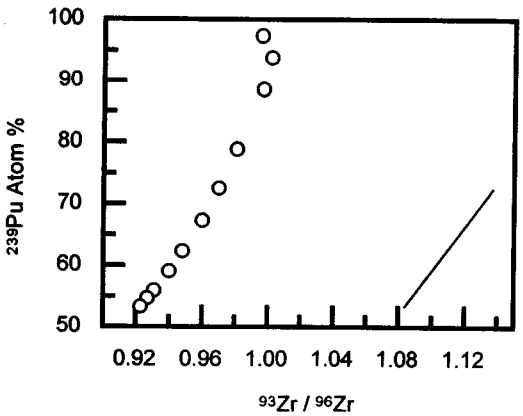

Fig. 4. Correlation between ^{239}Pu atom% and $^{93}Zr/^{96}Zr$ atom ratio; O : Calculated, ——: Experimental.