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Analysis of Irradiated ^{237}Np in the Experimental Fast Reactor JOYO for the Evaluation of its Transmutation Behavior in a Fast Reactor

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^{237}Np oxide targets irradiated in the experimental fast reactor JOYO were analyzed by applying sophisticated radiochemical technique. Pu and Np were isolated from the irradiated targets by anion exchange chromatography. Total fission events of each target were estimated by ^{137}Cs method. ^{237}Np and ^{236}Pu were determined by alpha spectrometry. The isotopic ratio of Pu and the content of Pu were determined by thermal ionization mass spectroscopy and isotope dilution mass spectrometry, respectively. From these analytical results, the transmutation behavior of ^{237}Np in a fast reactor was discussed. Up to about 528 EFPD (Effective Full Power Days) irradiation, the transformation through capture reaction was much larger than the incineration through fission reaction, although the latter increased comparatively in case of irradiation in hard neutron spectrum. ^{236}Pu was clearly observed in all irradiated ^{237}Np samples but its quantity was much smaller than the estimated value on the basis of present nuclear data library.

1. Introduction

The development of future nuclear fuel cycle system emphasized on fast reactor strategy is now under way in JNC (Japan Nuclear Cycle Development Institute).[1] In this nuclear cycle system, ^{237}Np is one of the target materials to be recovered from spent nuclear fuel and transmuted in a fast reactor core to reduce environmental impact caused by its long and high radiotoxity. MOX (U and Pu mixed oxide) fuel containing several percent of Np, which often includes other MA (minor actinides) such as Am and some FP (fission products), is considered as a promising candidate for the recycled fuel in fast reactors.[2, 3] This MA contained type MOX fuel is now developed in JNC and will be irradiated in the experimental fast reactor JOYO to evaluate the irradiation and transmutation behavior.[4] For the evaluation of transmutation behavior, a calculation code must be prepared on the basis of precise nuclear data with high accuracy. Pure ^{237}Np samples were fabricated and irradiated in JOYO partly for this purpose,[5] since the pure samples could eliminate the influence of ^{237}Np that was formed during irradiation from precedents such as ^{238}U and thus make the direct determination of MA transmuted from ^{237}Np possible.

Nuclear transformation chain started from ^{237}Np in a reactor is shown in Figure 1.[6, 7] The main neutron capture reaction of ^{237}Np leads to the formation of many Pu isotopes and the fast neutron induced (n,2n) reaction leads to the formation of long-lived nuclides, ^{236}Np, ^{236}U, and ^{236}Pu. The thermal fission cross section of ^{237}Np is only 2.15×10^{-2} b (10^{-28} m^2). Although the thermal fission cross section of ^{236}Np has not been measured so accurately, this nuclide is known for its very large thermal fission cross section of about 2500 b.[6] Thus, the determination of ^{236}Np in an irradiated Np sample is quite important, because several tens ppm of ^{236}Np in ^{237}Np affect greatly the fission property of a nuclear system including such Np.

The main objective of this study is the analysis of Pu and Np isotopes recovered from some ^{237}Np samples irradiated in JOYO. In this report, the radiochemical separation, the radioanalytical procedure, and its results are briefly described and the transmutation behavior of ^{237}Np in a fast reactor is discussed on the basis of present analysis.

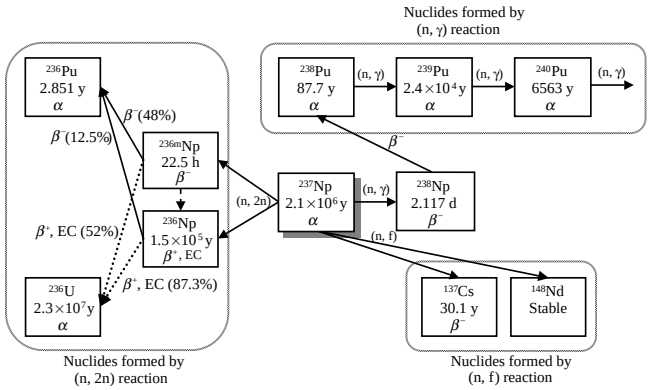

Figure 1. Nuclear reaction chain started from ^{237}Np.

2. Experimental

2.1. ^{237}Np Target for Irradiation. Figure 2 shows the positions of ^{237}Np samples loaded in JOYO. ^{237}Np dioxide powder was enclosed in a small (ϕ = 1.5 mm, length = 8 mm, weight = 70 mg) vanadium capsule and set in a central tube of irradiation rig as is shown in Figure 2. The B7 (un-instrumented fuel irradiation subassembly type-B No.7) which contained only one sample at the axial center of the subassembly was inserted in a core center region. The SMIR-15 (Structure Materials Irradiation Rig No.15) that contained three ^{237}Np samples, which were set in different axial position, was inserted in a stainless steel reflector region. Table 1 shows the specification and the irradiation condition of each ^{237}Np sample. Initial weight of ^{237}Np dioxide in each sample was about 0.2 mg. The B7 was irradiated for 190.392 EFPD (Effective Full Power Days) from September 5, 1986 to May 31, 1987. The SMIR-15 was irradiated for 527.958 EFPD from May 7, 1985 to

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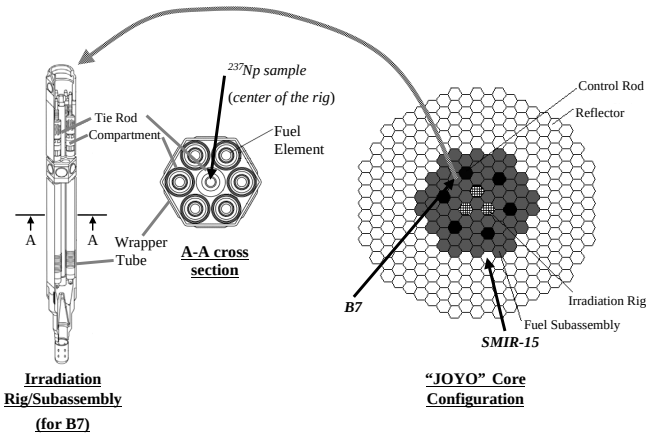

Figure 2. Loaded position of ^{237}Np sample in JOYO reactor.

TABLE 1: Specification and Irradiation Condition of ^{237}Np Sample

Assembly	Sample No.	Total fluence (n/m^2)	Axial position* (D.F.P.B. mm)	Initial weight of NpO_2 (μg)	Number of initial ^{237}Np atoms
SMIR-15	U	9.3×10^{26}	840	184	4.12×10^{17}
	C	7.9×19^{26}	573	186	4.16×10^{17}
	L	3.2×10^{26}	240	187	4.18×10^{17}
B7	C	5.5×10^{26}	775	192.5	4.31×10^{17}

*Distance from core bottom, Axial center: D.F.P.B.=775mm

February 1, 1989. Fast neutron fluence (E>0.1 MeV) for the sample at the axial center of the SMIR-15 was reported to be 7.9×10^{26} n/m^2.

2.2. Preliminary Estimation of Actinide Nuclides and Fission Products Formed in Each Sample. In order to see the actinide nuclides that were formed by neutron capture reaction and to design the analysis plan, the preliminary estimation of transformation and fission was carried out by using ORIGEN2 code.[8] Results are summarized in Table 2.

As shown in Table 2, each sample was expected to contain a considerable amount of ^{238}Pu, ^{239}Pu, ^{241}Pu, and ^{242}Pu. The isotopic composition of Pu was determined by thermal ionization mass spectrometry (TIMS) and used for evaluating the neutron capture reaction rate. In order to determine the total Pu content in an irradiated sample, isotope dilution mass spectroscopic technique was applied by using ^{242}Pu standard spike.

For the evaluation of total fission events in an irradiated sample, ^{137}Cs and ^{148}Nd monitoring method[9] are well established and used widely. ^{148}Nd method seems to be better than ^{137}Cs method in terms of accuracy. However, the amount of ^{148}Nd seems too small (about 80 ng at maximum) to analyze it by TIMS. Thus, ^{137}Cs method was selected for the estimation of total fission events.

^{236}Np and ^{236m}Np may become key nuclides for future nuclear transformation system including ^{237}Np. As described later, the direct determination of ^{236}Np was not successful for present analytical samples. Thus, ^{236}Pu was determined by alpha spectrometry and the result was used for the evaluation of effective ^{237}Np(n,2n)^{236m}Np cross section.

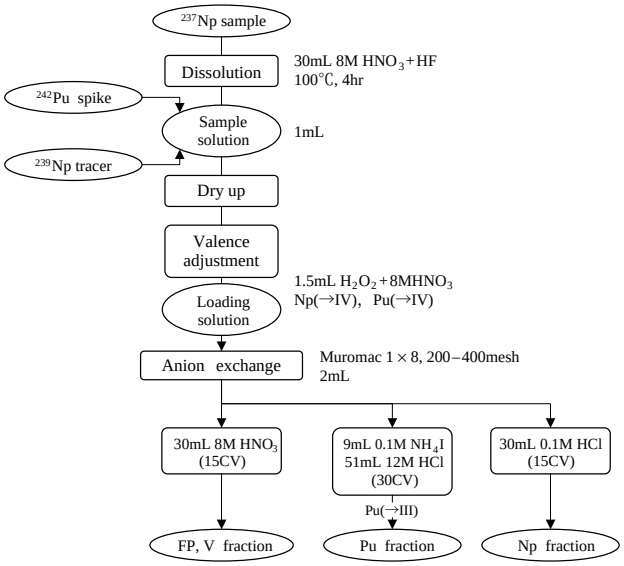

Figure 3. Flow sheet for chemical separation of irradiated ^{237}Np sample.

2.3. Experimental Procedure

2.3.1. Chemical Separation. In order to avoid the loss of analytical samples and to prepare the sample stock solution, a vanadium capsule together with the irradiated ^{237}Np oxide was dissolved directly in an 8 M (mol/dm^3) nitric acid solution by adding small quantity of hydrofluoric acid. A 0.1 mL aliquot of the sample stock solution was taken for gamma-ray spectrometry to determine ^{137}Cs. The chemical separation procedure is shown in Figure 3, which is principally the same, except the existence of vanadium, to that successfully applied to the analysis of Np and Pu in irradiated MOX fuel.[10] One mL of the sample stock solution was taken for actinides analysis. After the addition of ^{239}Np tracer, which was milked from ^{243}Am standard solution, the sample was dried up by gentle heating. The residue was dissolved in 1.5 mL of 8 M HNO_3 solution that contained a small quantity of H_2O_2 for the valence adjustment of Np and Pu to their tetravalent state and vanadium to its pentavalent state. Then, the solution was loaded into a small polypropylene tube column filled with 2 mL of Muromac 1x8 200~400 mesh (5 cm in column length). Np(IV) and Pu(IV) were adsorbed at the top of the column and the major fraction of fission products including rare earth elements and V(V) was eluted out from the column by washing with 30 mL of 8 M HNO_3. Then, the Pu fraction was eluted out from the column by washing with 60 mL of a mixed solution of 0.1 M NH_4I and 12 M HCl. Washing with 30 mL of 0.1 M HCl eluted out the Np fraction finally.

For the isotope dilution analysis of Pu, ^{242}Pu was spiked into the sample stock solution before the first dry up process of the present separation scheme.

In order to eliminate the interference of Pu on alpha spectrometry of Np, the separation of Pu from Np fraction was repeated twice to get the Np fraction pure enough for alpha spectrometry.

All chemical procedures were carried out in the airtight glove box settled in the Alpha-Gamma Facility (AGF) of O-arai Engineering Center of JNC.

TABLE 2: Number of Atoms for Each Nuclide in Irradiated ^{237}Np Calculated Preliminarily by ORIGEN2 Code[8]

Assembly	Sample No.	^{237}Np	^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu	^{242}Pu	^{241}Am	Am,Cm*)	^{236}Pu	^{236}Np	^{137}Cs	^{148}Nd
SMIR15	U	3.60E+17	9.40E+16	5.50E+15	2.10E+14	9.50E+12	1.60E+11	3.60E+11	1.40E+10	4.50E+12	5.30E+12	1.20E+15	3.40E+14
	C	3.80E+17	8.80E+16	4.60E+15	1.60E+14	6.40E+12	9.70E+10	2.40E+11	8.40E+09	3.90E+12	4.50E+12	1.00E+15	2.70E+14
	L	3.70E+17	1.10E+17	5.30E+15	2.60E+14	1.70E+13	3.30E+11	6.40E+11	2.60E+10	1.50E+12	1.90E+12	4.30E+14	1.20E+14
B7	C	4.60E+17	2.90E+16	5.40E+14	3.60E+12	2.00E+10	8.70E+07	1.30E+08	2.20E+06	4.70E+12	3.70E+12	8.10E+14	2.20E+14

*Summation of isotopes of Am (except ^{241}Am) and Cm

2.3.2. Alpha and Gamma-Ray Spectrometry. A multichannel pulse height analysis system, ORTEC Model 7800-8B2, was used to accumulate and analyze alpha or gamma-ray spectra. A silicon detector, ORTEC Model BA-017-200-300, and a planar high purity germanium detector, ORTEC Model GLP-16195/10-P, were used to take alpha and gamma-ray spectra, respectively.

2.3.3. Mass Spectrometry. A surface ionization mass spectrometer, Finigan Mat model MAT262 equipped with photon multiplier type detector and a six-channel Faraday cup detector was used for isotope analysis of Pu.

3. Results and Evaluation of Transmutation Behavior

Figure 4 shows an example of alpha spectrum of an isolated Np fraction. The alpha peaks of ^{237}Np are well separated from those of Pu isotopes. Figure 5 illustrates the observation of ^{236}Pu in an alpha spectrum of Pu fraction. Table 3 summarized the present analytical results expressed as the number of atoms for each nuclide in all samples. The figures in parentheses are relative errors (%) of 1σ criteria. Attempt to observe ^{236}Np by mass spectrometry was not successful. Thus, the data for ^{236}Np given in Table 3 were derived from the detection limit of mass spectrometry.

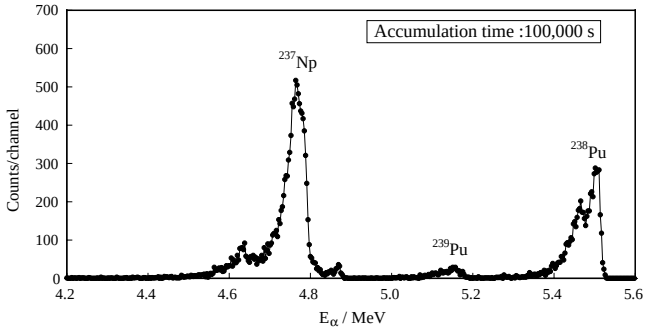

Figure 4. An example of alpha-spectra of isolated Np fraction.

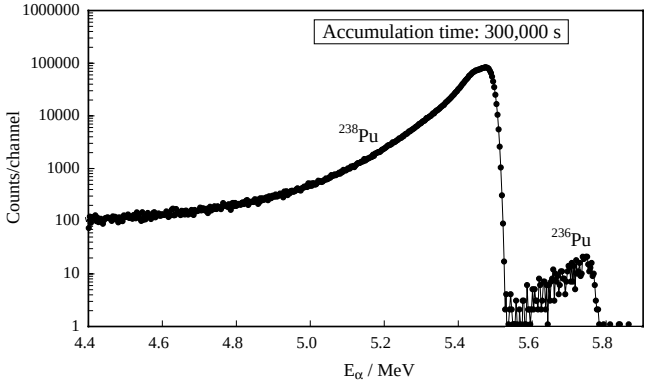

Figure 5. Alpha-spectrum of Pu fraction.

For the evaluation of transmutation behavior, the effective cross section data set is needed for capture and fission reaction of every actinide nuclides tabulated in Table 2. But, as is shown in Figure 2, the present irradiation assembly was quite complicated and heterogeneous. We have only limited information about the nuclides that undergo capture and fission reaction, namely ^{237}Np, ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, and ^{242}Pu. Thus, we selected rough proximate approach to evaluate the transmutation behavior from the present experimental data.

Total fission events were estimated by $N_f = 0.5 \times N_{Cs137}/EFY$, where N_{Cs137} is the number of ^{137}Cs atoms and EFY is effective fission yields. The effective fission yields are calculated by $EFY = \Sigma N_i \times FY_i/\Sigma N_i$, where N_i is the number of atoms for nuclide i at the end of irradiation and FY_i is the fission yield of 137 mass from nuclide i. This assumption does not introduce so much error to the evaluated total fission events, because the fission yield values for mass 137 from ^{237}Np, ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, and ^{242}Pu do not change so significantly.

The contribution of capture reaction was evaluated from the summation of all Pu atoms. In order to estimate the contribution of fast neutron reaction ^{237}Np(n,2n)^{236m}Np, it was assumed that all the ^{236m}Np decayed to ^{236}Pu without any reaction loss and the ^{236}Pu was produced uniquely through this pass, i.e., the production from ^{236}Np was ignored. These assumptions for the production of ^{236}Pu are appropriate because the life of ^{236m}Np is very short ($T_{1/2}$ = 22.5 h) and that of ^{236}Np is quite long ($T_{1/2}$ = 1500 y). Figure 6 shows the procedure for the evaluation of effective cross section of ^{237}Np(n,2n)^{236m}Np. The reaction yield of ^{236}Pu (C) was estimated by using trial effective 1-group cross section for ^{237}Np(n,2n)^{236m}Np reaction. The first trial 1-group cross section was calculated using 7-group of energy-dependent neutron flux and effective cross sections used in the MAGI code developed for the operation and management of JOYO.[11] The estimated yield of ^{236}Pu was

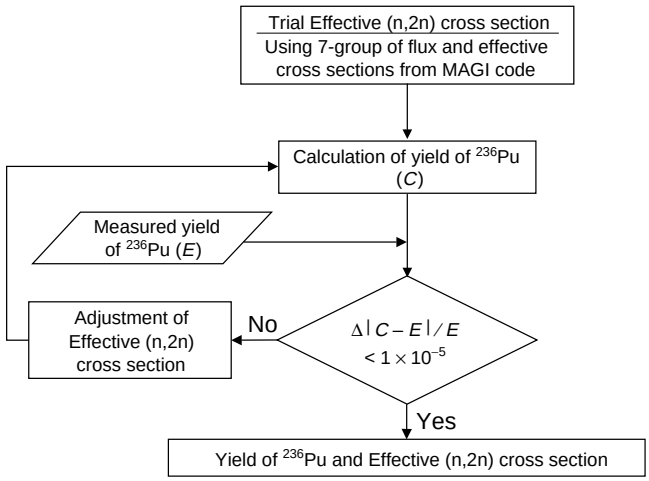

Figure 6. Procedure for the estimation of effective ^{237}Np(n,2n)^{236m}Np cross section.

TABLE 3: Analytical Results of Irradiated ^{237}Np Sample

Assembly	Sample No.	Initial ^{237}Np atoms	^{237}Np	^{238}Pu	^{239}Pu	^{240}Pu
SMIR-15	U	4.12E+17	3.41E+17 (1.4)	5.99E+16 (2.8)	2.38E+15 (2.8)	6.59E+13 (2.8)
	C	4.16E+17	3.23E+17 (1.8)	6.17E+16 (2.8)	2.57E+15 (2.8)	6.85E+13 (2.8)
	L	4.18E+17	3.14E+17 (1.2)	9.77E+16 (2.8)	5.86E+15 (2.8)	2.48E+14 (2.8)
B7	C	4.31E+17	3.85E+17 (2.2)	2.36E+16 (2.3)	3.68E+14 (2.2)	9.32E+12 (2.2)

Assembly	Sample No.	^{241}Pu	^{242}Pu	^{137}Cs	^{236}Pu	^{236}Np
SMIR-15	U	2.70E+12 (7.1)	5.21E+12 (4.9)	7.88E+14 (5.1)	4.71E+11 (4.2)	<3.99E+12
	C	2.20E+12 (8.1)	N.D. –	7.31E+14 (5.1)	4.07E+11 (5.0)	<4.99E+12
	L	3.32E+13 (2.9)	N.D. –	1.60E+14 (5.2)	7.31E+10 (6.1)	<4.07E+12
B7	C	2.26E+12 (2.2)	2.55E+12 (2.2)	5.04E+14 (5.1)	1.23E+12 (3.8)	<2.32E+12

TABLE 4: Calculated Results of Relative Contribution of Each Reaction Mode

Assembly	Sample No.	Atomic balance*1) Meas./qualified	Contribution of specified reaction mode(%)*2)			
			Fission	Capture	(n,2n)	Total
SMIR-15	U	1.02±0.04	3.58±0.20	15.52±0.46	(3.47±0.15)E-04	19.1±0.50
	C	0.97±0.04	3.46±0.20	16.67±0.51	(3.24±0.17)E-04	20.13±0.55
	L	1.02±0.03	0.72±0.04	25.51±0.73	(4.72±0.24)E-05	26.23±0.74
B7	C	0.98±0.06	2.33±0.15	6.1±0.18	(6.95±0.16)E-04	8.43±0.23

*1) Initial ^{237}Np atoms/(Residual ^{237}Np atoms + total Pu atoms + total fission events)
*2) Based on the number of the sum of residual ^{237}Np atoms, total Pu atoms and total fission events

compared with the measured yield (E). The estimation of effective 1-group cross section was repeated by adjusting mainly the energy dependent neutron flux until $\Delta|C-E|/E$ reached to 10^{-5}. The results of the evaluation of each reaction mode are summarized in Table 4.

4. Discussion

The summation of residual ^{237}Np atoms, total Pu atoms, and total fission events should be approximately equal to the initial number of ^{237}Np atoms. The ratio of the summation and the number of initial ^{237}Np atoms is given also in Table 4. As is clear in Table 4, the ratios are 0.97~1.02. This fact indicates that the present radiochemical analysis was carried out quite accurately and the rough approximation on the estimation for the contribution of capture reaction does not introduce so large error, i.e. fission of each Pu nuclide is smaller than its capture reaction.

Total fission events were found to be 0.7~3.6% of initial ^{237}Np, while capture products were 6.1~25.5% of the initial ^{237}Np. The contribution of capture was always larger than fission in each sample, while the ratio of fission to capture varied according to the sample loaded position.

Figure 7 shows the dependence of relative contribution of fission and capture on the axial irradiation position of SMIR-15 rig. The contribution of fission decreases simply from core to the bottom of fuel pin, while that of capture increases. This indicates the normal tendency of the neutron spectrum softening toward the both ends of fuel pin by the effect of reflector and structural materials. To see this effect in detail, fission to capture ratio is plotted as a function of fast neutron ratio, which was reported from management crew of JOYO,[11] in Figure 8. We can see clearly that the contribution of fission, which means incineration of ^{237}Np, increases greatly by the irradiation with hard neutron spectrum in a fast reactor.

Table 5 shows the estimated effective ^{237}Np(n,2n)^{236m}Np cross section together with that of JOYO cross section library,[12] which was reported as the mean value of each fuel pin. The estimated values are much smaller than the library value, as shown in Table 5. In spite of this finding, authors have no strong evidence to recommend presently evaluated cross section values. But, at least, this result reveals that there is either over-estimate of ^{237}Np(n,2n)^{236m}Np cross section or under-estimate of total cross section of ^{236}Pu in the present data library.

TABLE 5: Effective One-Group ^{237}Np(n,2n)^{236m}Np Cross-Section

Sample No.	Effective 1-group cross section (b) of ^{237}Np(n,2n)^{236m}Np	Estimated values of ^{236}Np** (atoms)	Estimated atom ratio of ^{236}Np/^{237}Np
SMIR-15 U	4.56E-05	6.15E+11	1.80E-06
SMIR-15 C	5.07E-05	5.49E+11	1.70E-06
SMIR-15 L	1.89E-05	9.22E+10	2.93E-07
B7 C	1.39E-04	1.08E+12	2.80E-06
JOYO *	3.47E-04	–	

* Values of "JOYO" cross-section library.[12]
**Values estimated from effective cross section ratio of ^{237}Np(n,2n)^{236m}Np/^{237}Np(n,2n)^{236}Np in JOYO ORIGEN2 library.[12]

The number of atoms of long lived ^{236}Np in Table 5 is calculated from the presently estimated effective cross section for ^{237}Np(n,2n)^{236m}Np assuming that the JOYO ORIGEN2 library data for the ratio of the cross section for ^{237}Np(n,2n)^{236}Np and ^{237}Np(n,2n)^{237m}Np is correct, i.e. 0.349.[12] As shown in Table 5, the content of long lived ^{236}Np in irradiated Np is supposed to be of ppm order. The presence of ^{236}Np in this order does not affect so much the fission characteristics of recovered Np. But, for the case of under-estimate of total cross section of ^{236}Pu, the content of ^{236}Np in the recovered Np sample is expected to be higher than 10 ppm and, thus, the macroscopic fission cross section of recovered Np will be affected by the presence of ^{236}Np.

This is the first experimental report that mentions the production of ^{236}Np and ^{236}Pu from ^{237}Np in a nuclear reactor. The authors consider that further experimental work is necessary to ensure the present finding of unexpected small production of ^{236}Pu on much strong experimental evidence. The

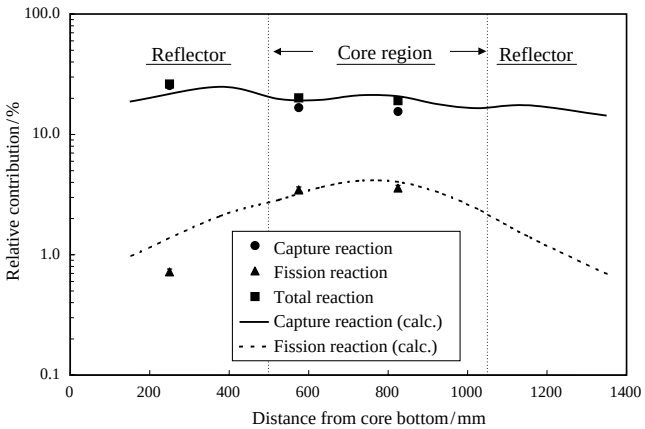

Figure 7. Change of relative contribution of capture and fission as a function of axial position for SMIR-15 rig.

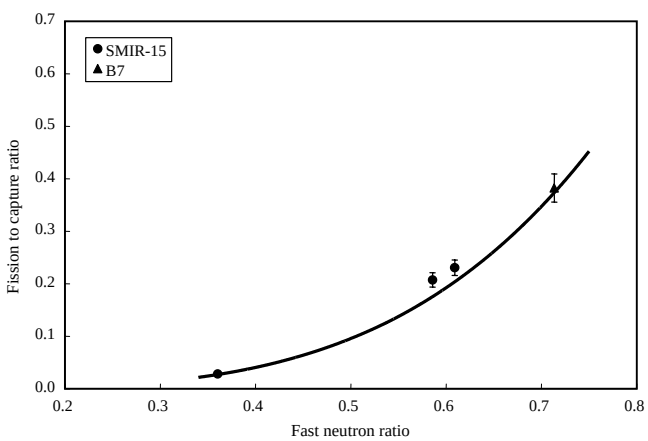

Figure 8. Change of fission to capture ratio as a function of fast neutron ratio.

isolated Np samples are stored in order to wait for the growth of ^{236}Pu from ^{236}Np in AGF. The result, the radiochemical determination of ^{236}Np in irradiated ^{237}Np, will be reported in near future.

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