THEORETICAL AND EXPERIMENTAL ANALYSIS OF IRRADIATED THORIUM BUNDLE FROM KAPS-2

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Abstract

Thorium bundles were loaded in Indian PHWRs for initial flux flattening from KAPS Unit 1 onwards. The Post Irradiation Examination was carried out for one of the discharged bundles from KAPS- Unit 2, which had seen 508 FPDs. About five grams of the irradiated bundle were cut off from the edge pellet of the outer ring of the irradiated 19-rod thorium cluster, and was supplied for dissolution studies and separation of the uranium isotopes. The isotopic vector of the bred uranium was assessed by three different techniques by three different groups in BARC. The burnup analysis using the stable fission products like Nd-148 burnup monitors was also carried out. The various independent experimental analyses showed the amount of ^{232}U to be about 490 ppm, which is nearly five times the originally predicted value by the ORIGEN-2 code (using the in built cross section library i.e. candunau.lib). A new set of effective one group cross sections for the nuclear reactions leading to the formation of ^{232}U was generated and calculations were repeated with ORIGEN. Also the lattice code CLUB was used with old WIMS (1971) and the latest IAEA (WLUP) 172 group libraries, to directly evaluate the uranium vector. More refined data sets and calculation models are required to improve the results further.

1. INTRODUCTION

Indian nuclear program envisages [1] extensive utilization of thorium for power production in the coming decades. The main stay of the Indian nuclear energy program has been the 220 MWe PHWRs based on 19-rod fuel bundle of natural uranium for the last three decades. In the early days, depleted uranium was used for flux flattening of PHWRs in the initial core. Later loading of ThO_2 bundles was adopted in Indian PHWRs (KAPS -1 onwards) to attain flux flattening [2]. This could accomplish the required power flattening in addition to reducing the requirement of 384 depleted bundles in the initial core to just 35 bundles of thorium oxide. A scattered loading was optimized to maximize the total power while preserving the worth of adjusters and the two shutdown systems. These bundles were discharged from the core as per the normal fueling program from about 150 Full Power Days (FPDs) to about 500 FPDs. Subsequently this loading has been adopted in all PHWRs (so far in 5 units). One of the discharged bundles from KAPS-2, which had seen 508 FPDs of irradiation in a central channel (at J-11-9), was brought to BARC for Post Irradiation Examination (PIE) analysis. A portion of this bundle was cut and dissolved for isotopic analysis by three different experimental groups.

Besides achieving the required flux flattening, thorium irradiation in PHWRs has given the experience in modeling the neutronic characteristics of thoria rods which is vital in the design of thoria based fuel. The PIE analysis is required to develop and validate physics codes required to study the growth of different actinides, its fission and decay with special emphasis on ^{232}U generation. The isotope ^{232}U has attracted special attention [4] in thorium fuel cycle as it has daughter products that emit strong gamma rays. The fabrication of ^{233}U fuel having more than a few ppm of ^{232}U would require remote fabrication and handling.

The formation of ^{232}U in thorium pins irradiated in PHWR mainly takes place by the following reactions:

$$^{232}Th\ (n, 2n)\ ^{231}Th\ (\beta^-)\ ^{231}Pa(n, \gamma)\ ^{232}Pa\ (\beta^-)\ ^{232}U$$

^{232}U is also formed in-situ with burn-up and thus ^{232}U is also formed in small amounts through the breeding reaction from ^{232}Th:

$$^{232}Th\ (n, \gamma)\ ^{233}Th\ (\beta^-)\ ^{233}Pa\ (\beta^-)\ ^{233}U(n, 2n)\ ^{232}U.$$
$$^{233}Pa\ (n, 2n)\ ^{232}Pa\ (\beta^-)\ ^{232}U$$

The production of ^{232}U is more in a harder spectrum because of the threshold nature of the ^{232}Th (n, 2n) reactions. Depending on the type of fuel, spectrum and burn-up, the fraction of ^{232}U produced can range from a few ppm to several hundreds of ppm.

Preliminary calculations using ORIGEN-2 code using the standard PHWR data base showed a ^{232}U concentration of about 80-100 PPM for the experimental bundle used in PIE. This was found to be in gross error with the experimental values obtained by actual chemical analysis. This may be because of the incompatibility of the nuclear data for the system under test. Even the currently available nuclear data of isotopes of thorium fuel cycle [3] are not yet on par with the status of nuclear data for uranium-plutonium fuel cycle. The development of a calculation method of effective one group cross sections taking the variation of neutron spectra as a function of neutron energy is important to conserve the reaction rates in the isotope burnup and depletion calculations performed by codes such as ORIGEN-2 [5]. This paper discusses the results of PIE and addresses the efforts to develop indigenous code system to predict the production of ^{232}U in thorium bundles irradiated in Indian PHWRs.

2. EXPERIMENTAL MEASUREMENTS:

2.1 Post Irradiation Examination Analysis

2.1.1 Dissolution of irradiated Thoria

About five grams of the irradiated bundle were cut off in powder form from the edge pellet of the outer ring of the irradiated 19-rod cluster by Post Irradiation Examination Division and was transferred into a shielded container. Known quantity of the oxide by weight was taken into the dissolution set up housed inside a shielded glove box assembly at Fuel Reprocessing Division. 25 ml of the dissolvent mixture of 13 M HNO_3, 0.03 M of HF and 0.1 M of $Al(NO_3)_3$ was added for dissolving the oxide. Heating to boiling was carried out using thermo-mantle. Periodical samples were drawn to ensure complete dissolution. After 16 hours, ensuring constant thorium concentration in two consecutive samples, the solution was transferred to a 25 ml volumetric flask and total weight of the solution was noted.

2.1.2 Estimation of uranium, thorium and isotopic composition of uranium

Aliquots were drawn from this solution for mixing with respective spikes and also for the isotopic composition determination of U. The spike solution was calibrated against chemical assay standards. Spiked aliquots were treated for proper chemical exchange between the spike and the sample isotopes. Samples were loaded on to the vaporization filament of a double rhenium filament assembly. A Thermal Ionization Mass Spectrometer (TIMS) with multi-collector system was employed for carrying out the mass spectrometric analyses.

A different sample from the same source was independently dissolved. Uranium was purified from spiked and unspiked samples by anion exchange (Dowex 1x8) in 10M HCl [7] and was analysed by TIMS for uranium concentration and isotopic content .

^{232}U content in the sample was analysed by alpha spectrometry due to the probable interference of ^{232}Th in mass spectrometric analysis. Uranium was purified by a solvent extraction procedure developed in-house [7]. This method uses a separation procedure using TOPO in xylene for the purification of uranium from other alpha emitters. TOPO layer is evaporated on an SS disc and counted in an alpha spectrometer. Counting is carried out under a vacuum of better than 5×10^{-2} mbar to avoid energy degradation. Spectra evaluation procedure followed has been explained in detail in an earlier report [8].

Concentration of Th was determined by EDTA titration using xylenol orange indicator [9]and also by spectrophotometric method using thoron [10].

2.1.3 Burnup Estimation

(a) ^{148}Nd dtermination by Thermal Ionization Mass Spectrometry

The non-retained fission products fractions obtained from the ion exchanger column used for the separation of uranium were collected from ^{142}Nd spiked and unspiked samples. Nd contained in it was purified by loading on Bio-Rad 1x2 anion exchange column in a mixed solvent medium of (HNO_3 + MeOH) [11]. Purified fractions were loaded on to the vaporization filament of double rhenium filament assembly. Spiked as well as unspiked samples were analysed for the determination of concentration and isotopic compositions respectively using TIMS.

Purified fractions of the spiked mixture were analysed for the $^{142}Nd/^{148}Nd$ ratio after correcting for natural contamination for 142Nd. From the fission yield of ^{148}Nd, burnup was calculated.

(b) Fission products Estimation by Gamma Counting

Dilute solution of the irradiated fuel was assayed by direct gamma ray spectrometry. The counting time for the samples was adjusted to get better than 1% statistics for gamma ray peak areas. Long lived fission products, ^{106}Ru, ^{125}Sb, $^{134,137}Cs$, and ^{144}Ce were identified and assayed. The gamma ray spectra were analyzed by using the SAMPO program. The disintegration rates of the fission products at the end of the irradiation was calculated using their count rates, gamma ray abundances, cooling time and the respective efficiency values. The total number of fissions per ton of thorium was calculated using the thorium analysis data.

3. GENERATION OF NEW DATA FOR USE WITH ORIGEN FOR IRRADIATION OF THORIUM.

The first calculations [6] using ORIGEN-2 code and its CANDU PHWR database showed large discrepancies for ^{232}U / ^{233}U ratio between experiments and

calculations for thorium irradiated in Indian PHWR. This is because the flux spectrum may not exactly match with the flux spectrum in our location of interest. In principle, generation for each time step for a given irradiation location in our reactor system, the effective (self-shielded) multigroup and one group cross sections defined by

$$\sigma = \frac{\sum_{g=1}^{NG} \sigma_g \phi_g}{\sum_{g=1}^{NG} \phi_g}$$

for each nuclide and for each reaction is to be generated. Here ϕ_g is the flux of the g^{th} group in the WIMS 69 / 172 energy group structure and σ_g is the effective (self-shielded) multi-group cross section for the group 'g'. The appearance of several stable and radioactive nuclides is to be taken into account for different neutron spectra as a function of time in various rings of thorium rods. The current version of the PREPRO code [13], has been employed by us to calculate effective one group cross sections. These calculations were performed for only those reactions not available in the lattice calculations.

The σ_g values are obtained by processing ENDF/B-VI.8 for nuclear reactions of interest. The generation of effective, resonance shielded one-group fission and absorption cross-sections of ^{232}Th, ^{233}U and ^{233}Pa are provided by the CLUB code [15-16] using 69 group WIMS – 1971 cross section library. The calculations were performed in two steps. In the first step, lattice cell calculations were performed at various burnups for normal cell containing natural UO_2 fuel. The multigroup cell cross-sections were homogenized at each burnup. In the second step, the calculations were performed for lattice cell containing thorium bundle surrounded by 8 lattice cells containing UO_2 fuel homogenized in the first step at a burnup of 3500 MWD/T. The burnup calculations for thorium bundles were done by assuming a constant value of flux (average one group)of 2.3×10^{14} n/cm^2-s[20]in the fuel. Our calculations use 500FPDs.

The calculations of flux spectra were also performed using ENDF/B-VI.8 library in both 69 and 172 groups but in single cluster model for thorium bundle using the PHANTOM code [17-18] that incorporates the CLUB module. The values in ORIGEN system are from its associated library "Candunau.lib". These values of cross sections are based upon ENDF/B-IV or -V. The cross sections in CLUB are based upon the 1971 WIMS library and are available only for absorption and fission processes in ^{233}U, ^{232}Th and for absorption process in ^{233}Pa. The (n, 2n) reaction is not explicitly available in the WIMS convention. The larger values in ORIGEN for ^{232}Th(n, γ) and ^{233}U(n, γ) and ^{233}U(n, f) relative to WIMS-1971 may indicate that these cross sections in ORIGEN may not be resonance self-shielded in addition to being based upon a different basic evaluated data file.

Attempt was made to estimate the above cross-section using 172 group averaged one group effective (n, 2n) cross-section for ^{232}Th . This value is 31%

larger than the 69 group value. The effective value is determined by the percentage of flux above the (n, 2n) threshold (-6.34MeV in ENDF/B-VI.8). The super cell model gives a value (0.1%) in the beginning of burnup but goes to around 0.5% at the end of 500 days. The calculated value of relative flux in the first group is sensitive to the model of the lattice used. The single cluster model of thorium bundle even at zero burnup gives a larger relative flux in the first group of 0.3% and at the end of 500 days, 0.5%. We observe that the energy variations of neutron spectrum in the two models nearly converge at large burn-up to give the same relative flux in the first group. This is expected as ^{233}U keeps building up in thorium as a function of time during irradiation.

A general observation is that the cross sections in ORIGEN database are very large for ^{233}U (n, γ), ^{233}U (n, f) and ^{232}Th (n, γ) cross sections. This cross section influences the ^{232}U production from ^{233}U only in cases where ^{233}U is initially present in significant quantities. In present case of irradiation of thorium, this reaction rate does not dominate in producing ^{232}U since the number of atoms of ^{233}U are much smaller than the number of ^{232}Th atoms. The 1971 WIMS library treats the fission cross section of ^{233}Pa as zero. The new fission cross sections are four times larger than in the ORIGEN-2 library.

4. RESULTS OF SENSITIVITY CALCULATIONS TO CODES AND BASIC DATA.

Table- 3 gives a comparison of various calculations and measurements for the ratio of ^{232}U to ^{233}U in weight ppm. The calculations at this time do not include analyses of history of irradiation. The last but 2 columns show the efforts to make comparisons using 69 and 172 group cross sections using WIMS library. The last column uses the ORIGEN approach for (n, 2n) cross sections. The way to calculate production of ^{232}U in WIMSD code is to treat the formation of ^{231}Pa as a pseudo-fission product of ^{232}Th by specifying the yield of ^{231}Pa as the ratio of (n, 2n) cross section of ^{232}Th to the fission cross section of ^{232}Th. This ratio is evaluated, however, for a specified spectrum and the value (0.185 in this case) placed in WIMS library. Therefore an approach followed by the WIMS convention gives, as long as this ratio is fixed, essentially the same ^{232}U production for any other spectra or number of groups. Our ORIGEN calculations do show, as illustrated in Table-3, different values of production of ^{232}U consistently as the one group ^{232}Th(n, 2n) cross sections are different in 69 and 172 groups.

In Table- 2, presented are the C/E values for the isotopes of uranium. The calculations at this time do not include analyses of history of irradiation conditions to specify the flux level more accurately.

The results with ENDF/B-VI.8 based 69 and 172 group WIMSD libraries in Table-2 correspond to the use of single cell option. The (n, 2n) modeling is performed using ORIGEN outside CLUB code as WIMS convention does not treat this reaction explicitly.

Table 3. shows the total number of fissions per ton of thorium as obtained from gamma spectrometric analysis. Burnup estimation from this data gives a value of 10800 MWD/T. The ^{148}Nd data showed a burnup value of 1.251 atom % which when converted to MWD/T gives a value of 12510 MWD/ T.

5. CONCLUSIONS

The three independent experimental measurements agreed very well between them. It is also planned to analyse experimentally different sections of the current fuel bundle, as well as fuel bundles of different irradiations in the near future.

A methodology to update database of effective one group cross sections was evolved for use with the ORIGEN code. Analyses of isotopic compositions in thorium bundles irradiated in Indian PHWR was performed with different cross section sets and methods of analyses to see the sensitivity to calculated values of isotopic content. It is found by sensitivity calculations that the one-group cross-sections are very sensitive to flux modeling as well as the cross section database used. The prediction of ^{232}U is sensitive to the number of groups in the MeV region. More detailed analysis with 172 group WIMS library at the lattice stage (single and super cell models) and consistent core follow up scheme are being done, and the initial results are quite encouraging. [21].

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Table -1
Dissolver solution fission product analysis

S.No.	Nuclide	Activity per g of the dissolver solution at the end of irradiation	Activity per Ton of thorium at the end of irradiation	No. of Fissions / Ton of Thorium
1.	^{106}Ru	$(1.93 \pm 0.07) \times 10^{6}$	9.84×10^{14}	2.73×10^{25}
2.	^{125}Sb	$(3.91 \pm 0.02) \times 10^{5}$	1.99×10^{14}	2.69×10^{25}
3.	^{134}Cs	$(1.69 \pm 0.01) \times 10^{6}$	8.62×10^{14}	--
4.	^{137}Cs	$(2.90 \pm 0.02) \times 10^{6}$	1.48×10^{15}	3.02×10^{25}
5.	^{144}Ce	$(4.90 \pm 0.04) \times 10^{7}$	2.50×10^{16}	3.33×10^{25}
No. of fissions per metric Ton of thorium = $(2.94 \pm 0.30) \times 10^{25}$ = 10800.0 MWD				

Table - 2

The ratio (C/E=Calculation/Experiment) for isotopic contents in weight for thorium bundles irradiated in PHWR.

Isotope	Flux = 2.3×10^{14} n. cm^{-2}. s^{-1}			
	ORIGEN-2	CLUB super cell WIMS1971 library 69 groups	ENDF/ B-VI.8 PHANTOM Single Cluster Model	
			69groups	172groups
^{232}U	0.418	1.07(ORIGEN2)	1.02	1.02 1.33(ORIGEN)
^{233}U	1.47	1.02	0.97	0.97
^{234}U	2.73	1.1	0.83	0.83
^{235}U	2.48	1.07	0.77	0.78
^{236}U	2.35	1.08	0.62	0.62

Table - 3

Calculated to Experimetal (C/E) Ratio of ^{232}U to ^{233}U in weight ppm

$$\sum_{g=1}^{NG} \phi_g = \textbf{Total flux} = \phi \text{ (n/cm}^2\text{/sec)}$$

$\phi = 2.3 \times 10^{14}$				
ORIGEN-2 and Candunau.lib	ORIGEN-2 Super Cell Model WIMS1971 data ; Updated cross sections	ENDF/B-VI.8 WIMSD Library from WLUP, PHANTOM, Single cluster model		
		69 Groups	172	172 Groups ORIGEN
0.29	1.17	1.08	1.08	1.401