Estimate of Neutron Fluence Using Isotope Ratio Method for ZR-2.5NB Materials Irradiated in the National Research Universal Reactor

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The isotope ratio method (IRM) is a technique used for estimating the energy production in a fission reactor by measuring isotope ratios in nonfuel reactor components. This method has been successfully demonstrated on the estimation of cumulative energy production as well as plutonium production in graphite-moderated and light-water-moderated reactors for nonproliferation purposes. In this paper, IRM was used to estimate neutron fluence in Zr-2.5Nb materials irradiated in fast neutron (FN) irradiation facilities in the National Research Universal (NRU) reactor. Neutron fluence has been shown to be an important parameter for studying irradiation effects on the performance and properties of critical reactor components. Selected isotope ratios of hafnium and iron were used as indicators of the neutron fluence in Zr-2.5Nb sample materials. Correlations between neutron fluence and the indicator element isotope ratios were generated using the reactor physics simulation codes Winfrith improved multigroup scheme (WIMS)-AECL and SCALE/Oak Ridge Isotope GENeration code (ORIGEN). Inductively coupled plasma-mass spectrometry (ICP-MS) was used to obtain accurate measurements of the isotope ratios. Neutron fluence values estimated using IRM, were in good agreement with the values based on measured irradiation power histories of the NRU reactor. This study proposes a potential application of IRM to the estimation of neutron fluence for critical reactor components in heavy-water-moderated reactors such as pressure and calandria tubes in CANDU® reactors. [DOI: 10.1115/1.4055931]

Keywords: neutron fluence, WIMS, TRIAD, ORIGEN, NRU, IRM

1 Introduction

Neutron fluence, the time integral of neutron flux, is an important parameter used to understand the effects of irradiation damage on the performance and properties of reactor materials and to assess the changes to the predicted service life of critical reactor components, such as pressure and calandria tubes in CANDU reactors [1]. However, obtaining accurate neutron fluence values requires irradiation histories or in-core measurement, which is unavailable in most cases. A method that can estimate neutron fluence without requiring irradiation histories will offer significant benefits for the studies of the effects of irradiation on materials.

In this paper, the isotope ratio method (IRM) was used to estimate neutron fluence in Zr-2.5Nb materials irradiated in fast neutron (FN) irradiation facilities in the NRU reactor [2], a heavy-water-cooled and -moderated reactor with a well-thermalized neutron spectrum similar to that of CANDU reactors. The NRU FN irradiation facilities were used to supply fast neutrons (>1 MeV) to experiments studying the effects of irradiation on creep, irradiation growth, stress-relaxation and corrosion of reactor materials, mainly pressure or calandria tubes in CANDU reactors. The FN rod design consists of an inner cavity, capable of holding experimental sample holders loaded with material specimens, surrounded by a cooled annulus containing 15 natural or enriched UO_2 fuel elements. A cutaway view of the FN irradiation facility and the cross section of the experimental assembly are illustrated in Fig. 1.

The isotope ratio method is a technique used for estimating the energy production in a fission reactor by measuring indicator element isotope ratios in nonfuel reactor components [3]. The indicator element isotope ratios can be correlated with the cumulative energy production and subsequently other related physics parameters, such as neutron fluence and plutonium production, using reactor physics simulation methods. The IRM method has been successfully demonstrated on the estimation of cumulative energy production as well as plutonium production in graphite-moderated and light-water-moderated reactors for nonproliferation purposes [4,5].

The objective of this study is to assess the feasibility of IRM in estimating neutron fluence in reactor components within reasonable accuracies. The neutron fluence in the Zr-2.5Nb samples estimated by IRM was compared with the fluence calculated through the NRU reactor core-simulation and core-following code suite, Winfrith Improved Multigroup Scheme/TRIAngular-Dioscontinuity-factor-three-dimensional (WIMS/TRIAD) [6,7], based on actual irradiation power histories.

2 Assessment of Isotope Ratio Method in the Estimation of Neutron Fluence

The process of assessing the IRM for estimation of neutron fluence follows these steps:

- selecting material samples with accurate irradiation histories
- selecting candidate fluence-indicator-element isotope ratios
- generating correlations between indicator element isotope ratios and neutron fluence using reactor physics simulation methods
- measuring indicator element isotope ratios using Inductively coupled plasma-mass spectrometry (ICP-MS)
- comparing neutron fluence estimated using IRM with measured values

The material samples used in this study were sectioned from thin Zr-2.5Nb bars that were irradiated in sample holders within an NRU FN rod facility for the purpose of monitoring the evolution of microstructural damage due to neutron fluence. The irradiation phases associated with the Zr-2.5Nb samples are summarized in Table 1. The results of material test report for the Zr-2.5Nb samples used in this study are summarized in Table 2.

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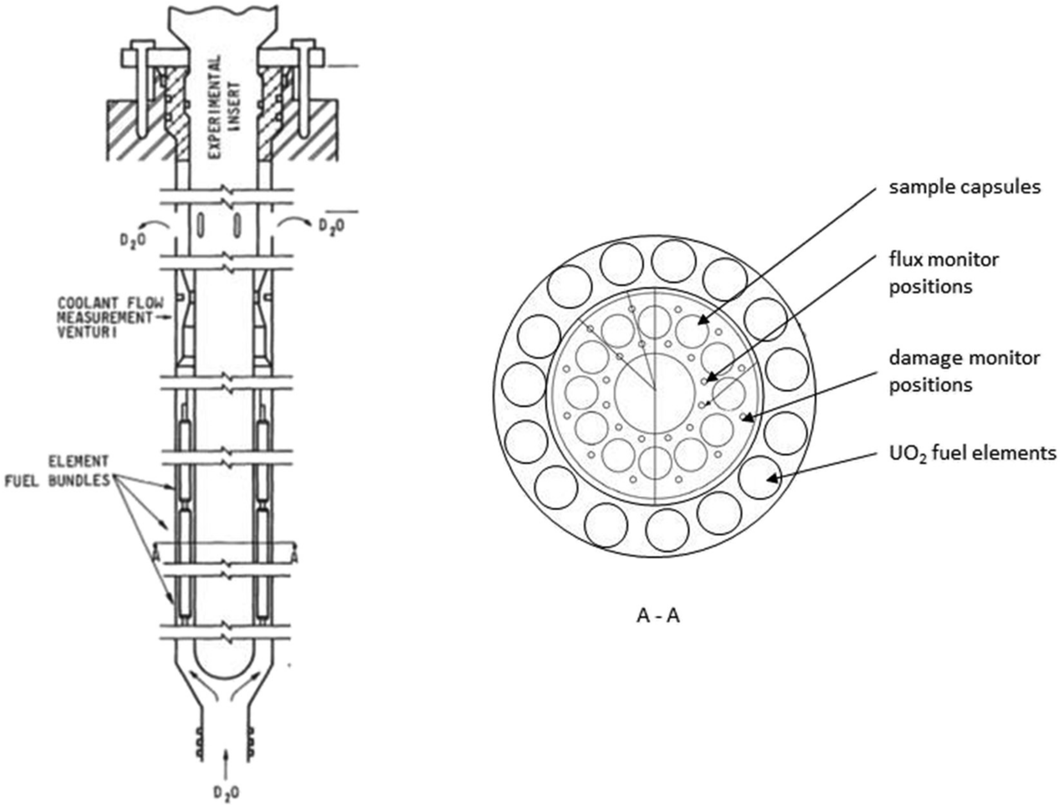

Fig. 1 Cutaway view of NRU FN irradiation facility and cross section of fueled region [2]

The indicator elements used in IRM were selected based on the following considerations: they have stable isotopes generated from neutron activation reactions, their respective isotope ratios are highly sensitive to neutron fluence in the range of interest, and they appear with sufficient concentrations allowing accurate measurements.

The candidate fluence indicator elements for the Zr-2.5Nb material irradiated in FN rods in the NRU reactor and their relevant isotope ratios are listed in Table 3.

2.1 Neutron Fluence Calculated by TRIAD.

Winfrith improved multigroup scheme/TRIAD, the core-simulation and core-following code suite for NRU, was used to track locations, power, and burnup of fuel assemblies, as well as to calculate flux distributions in the NRU reactor core. The code suite was validated using measured neutron flux, and the average bias of code predictions was shown to be less than 2% of measured values [7]. Therefore, neutron fluence values calculated based on TRIAD calculated flux and actual irradiation histories are considered as measured values in this paper.

The measured neutron fluence values of the Zr-2.5Nb samples are obtained based on the following:

- the measured irradiation power histories for the FN rods
- the flux distributions along the FN rods calculated using TRIAD
- the fluxes in FN rod damage monitors calculated using neutron transport code WIMS-AECL [6]

Table 1 Irradiation phases of Zr-2.5Nb samples

Irradiation phase Irradiation time (h)	Phase 1 4315	Phase 2 4164	Phase 3 3960
CG84E	×	×	×
CJ85E		×	×
CG82E-1	×	×	
CG82E-2	×	×	
CJ84E-1		×	
CJ84E-2		×	

Table 2 Material test report material compositions

	Specification		
Element	Min	Max	Measured[a]
Al (Aluminum)	—	0.0075	0.0034 ± 0.0001
B (Boron)	—	0.00005	<0.00002
C (Carbon)	—	0.027	0.011 ± 0.001
Cd (Cadmium)	—	0.00005	<0.00002
Co (Cobalt)	—	0.002	<0.0010
Cr (Chromium)	—	0.02	<0.0100
Cu (Copper)	—	0.005	<0.0025
Fe (Iron)	—	0.15	0.043 ± 0.002
H (Hydrogen)	—	0.0025	0.0005 ± 0.0001
Hf (Hafnium)	—	0.01	0.0042 ± 0.0002
Mg (Magnesium)	—	0.00	<0.0010
Mn (Manganese)	—	0.005	<0.0025
Mo (Molybneum)	—	0.01	<0.0025
N (Nitrogen)	—	0.01	0.0027 ± 0.0004
Nb (Niobium)	2.40	2.80	2.60 ± 0.04
Ni (Nickel)	—	0.01	<0.0035
O (Oxygen)	0.09	0.13	0.11 ± 0.01
Si (Silicon)	—	0.01	0.0025 ± 0.0005
Sn (Tin)	—	0.01	<0.0025
U (Uranium)	—	0.00035	<0.0001
W (Tungsten)	—	0.01	<0.0025
Zr (Zirconium)	Balance		balance

[a] "<" entries indicate analyzed levels were below established detection limit. Uncertainties correspond to one standard deviation on three assay measurements.

Table 3 Candidate indicator elements, isotopes and isotope ratios

Indicator element	Isotope	Isotope ratio
B (Boron)	^{10}B, ^{11}B	^{10}B/^{11}B
Cd (Cadmium)	^{110}Cd, ^{111}Cd, ^{112}Cd, ^{114}Cd, ^{116}Cd	^{110}Cd/^{114}Cd, ^{111}Cd/^{114}Cd, ^{112}Cd/^{114}Cd, ^{114}Cd/^{116}Cd
Cr (Chromium)	^{50}Cr, ^{52}Cr, ^{53}Cr, ^{54}Cr	^{50}Cr/^{54}Cr, ^{52}Cr/^{54}Cr, ^{53}Cr/^{54}Cr
Fe (Iron)	^{56}Fe, ^{57}Fe	^{56}Fe /^{57}Fe
Ni (Nickel)	^{60}Ni, ^{61}Ni, ^{62}Ni	^{60}Ni/^{61}Ni, ^{61}Ni/^{62}Ni
Nb (Niobium)	^{93}Nb, ^{94}Nb	^{93}Nb/^{94}Nb
Sn (Tin)	^{115}Sn, ^{117}Sn, ^{118}Sn, ^{119}Sn	^{115}Sn /^{117}Sn, ^{115}Sn /^{118}Sn, ^{115}Sn /^{119}Sn
Hf (Hafnium)	^{176}Hf, ^{177}Hf, ^{178}Hf, ^{179}Hf, ^{180}Hf	^{176}Hf /^{177}Hf, ^{178}Hf /^{177}Hf, ^{179}Hf /^{177}Hf, ^{180}Hf /^{177}Hf
W (Tungsten)	^{182}W, ^{184}W	^{184}W/^{182}W
U (Uranium)	^{235}U, ^{236}U, ^{238}U	^{235}U/^{238}U, ^{236}U/^{238}U

The neutron fluence values for the Zr-2.5Nb samples are calculated using

$$F = \sum_{i=1}^{I} F_i = \sum_{i=1}^{I} (\varnothing_i \times t_i) \tag{1}$$

where

F total neutron fluence, n/cm^2

F_i fluence accumulated over the irradiation period i, n/cm^2

I total number of irradiation periods

$\varnothing_i$ average neutron flux in damage monitor during irradiation time period i, n/cm^2·s

t_i irradiation time duration for the irradiation period i during which the neutron spectrumis considered unchanged, s

The average neutron flux in the damage monitor during the irradiation time period i is calculated as

$$\varnothing_i = \frac{LP_{\text{mea},i}}{LP_{\text{TRIAD},i}} \times \varnothing_{\text{TRIAD},c,i} \times \frac{\varnothing_{WIMS,\text{dm},i}}{\varnothing_{WIMS,c,i}} \tag{2}$$

where

$LP_{\text{mea},i}$ is measured FN rod linear power averaged over irradiation time period i, MW/m.

$LP_{\text{TRIAD},i}$ is TRIAD calculated FN rod linear power averaged over irradiation time period i, MW/m.

$\varnothing_{\text{TRIAD},c,i}$ is TRIAD calculated FN cell neutron flux in irradiation time period i, n/cm^2·s.

$\varnothing_{\text{WIMS},\text{dm},i}$ is WIMS calculated flux in the damage monitor in irradiation time period i, n/cm^2·s.

$\varnothing_{\text{WIMS},c,i}$ is WIMS calculated FN rod cell flux in irradiation time period i, n/cm^2·s.

2.2 Correlation Between Indicator Element Isotope Ratios and Neutron Fluence. The correlations between indicator element isotope ratios and neutron fluence were generated using WIMS-AECL 3.1.3.1 and Oak Ridge Isotope GENeration code (ORIGEN) version 2.2 [8]. WIMS-AECL, a two-dimensional multigroup neutron transport code used for reactor lattice calculations, was used to model the FN rod irradiation in the NRU reactor to generate neutron spectra and fluxes as functions of irradiation time or fuel burnup. Next, neutron cross sections were generated using the COUPLE module [9] in ORIGEN based on the WIMS calculated spectra and fluxes. Time-dependent isotope concentrations were then calculated using ORIGEN 2.2, which calculates time-dependent concentrations, activities and radiation source terms for a large number of isotopes simultaneously generated or depleted by transmutation, fission, activation, and radioactive decay.

Figure 2 illustrates the neutron spectra in the Zr-2.5Nb damage monitors at different irradiation times ranging from 0 to 1200 days, which correspond to different fuel burnups in NRU FN rod fuels. It shows that the neutron spectra in Zr-2.5Nb materials are relatively insensitive to irradiation time and fuel burnup. Therefore, one or a few spectra are sufficient to represent the sample spectra for the whole irradiation period.

Figures 3 and 4 illustrate the correlations between the selected indicator isotope ratios and neutron fluence. The selected isotope ratios are sensitive to neutron fluence, which makes them good candidate indicators provided they can be measured within sufficient accuracy.

2.3 Isotope Ratio Measurements Using ICP-MS. Experimental determination of stable isotope ratios is usually done by mass spectrometry [10].

With the significant change of element isotope ratios (listed in Table 3) expected from the naturally occurring isotopic ratios prior to neutron irradiation, ICP-MS is the preferred technique to measure postirradiation isotope ratios due to its speed, low cost, high accuracy, and direct analysis of dissolved samples without the requirement to remove a sample's Zr-Nb matrix. Additionally, CNL has an ICP-MS facility that is capable of processing radioactive materials [11].

Iron and hafnium were identified to be the most promising indicator elements as Fe is a minor alloying additive. Hf is a consistent impurity in the Zr-2.5Nb materials (Table 4), and their isotope ratios can be accurately measured based on the capability of ICP-MS. Although ^{93}Nb/^{94}Nb is sensitive to neutron fluence, it was not feasible to be measured using ICP-MS due to the strong interference from ^{94}Zr. Other element isotope ratios such as boron, cadmium, and tin were not selected due to their low concentrations in Zr-2.5Nb alloy resulting in insufficient measurement accuracy, or due to interference from isotopes with same atomic mass.

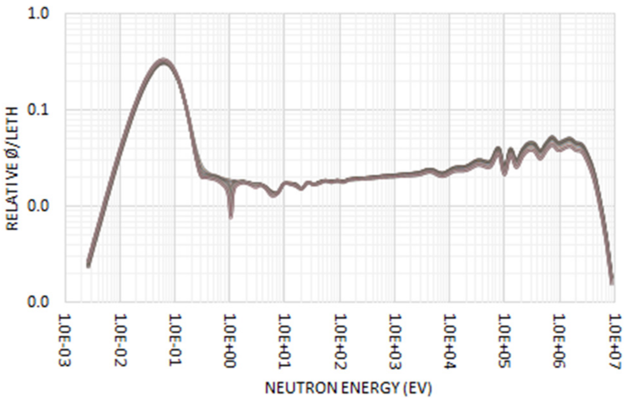

Fig. 2 Neutron spectra in Zr-2.5Nb damage monitor during irradiation

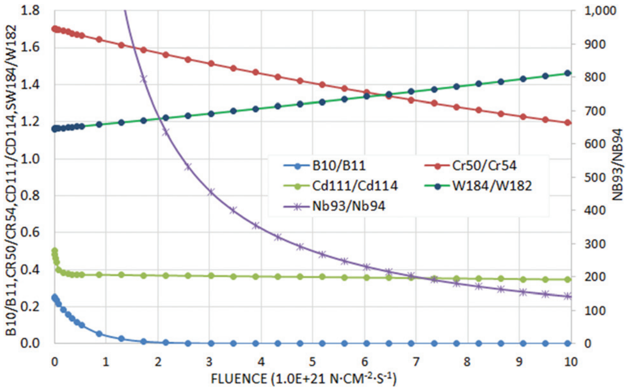

Fig. 3 Selected indicator isotope ratios-I

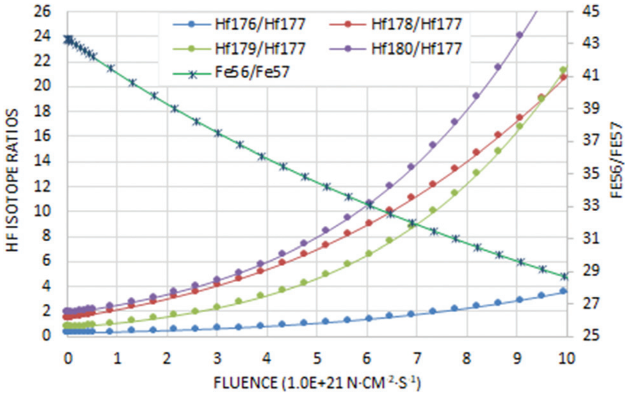

Fig. 4 Selected indicator isotope ratios-II

The concentration of hafnium as an impurity in Zr-2.5Nb alloy is significantly higher than those of the other elements with atomic masses in the range of 176 to 179; i.e., Yb, Lu, Ta, and W. Therefore, the interference from these elements and their neutron activation products on the measurement results is minimal. Furthermore, all the radionuclides of Lu, Ta, and W with atomic masses ranging from 176 to 179 are short-lived except for ^{179}Ta, which has a half-life of 1.82 years. ORIGEN calculation results show that the quantity of ^{179}Ta in the Zr-2.5Nb samples is ten orders of magnitude smaller than that of ^{179}Hf. Another potential interference is the Zr dimer ion ^{90}Zr^{90}Zr^{+} on ^{180}Hf^{+}. However, the formation of the ^{90}Zr^{90}Zr^{+} species was not observed in ICP-MS tests with pure Zr solution. Therefore, ICP-MS can be used directly to analyze the selected hafnium isotope ratios accurately in Zr-2.5Nb samples with no concern regarding interference.

Of the four stable isotopes of iron, only ^{56}Fe and ^{57}Fe are free from interference of other stable isotopes and they are only overlapped by relatively short-lived nuclides ^{56}Co, ^{57}Co, ^{56}Ni, and ^{57}Ni. These interfering isotopes have a diminishing effect on the accuracy of the ^{56}Fe/^{57}Fe isotope ratio with increasing decay time. ORIGEN calculation results confirm that ^{57}Co in the Zr-2.5Nb samples is seven orders of magnitude less than ^{57}Fe, and there is hardly any trace of ^{56}Co, ^{56}Ni, or ^{57}Ni in the Zr-2.5Nb samples due to their short half-lives.

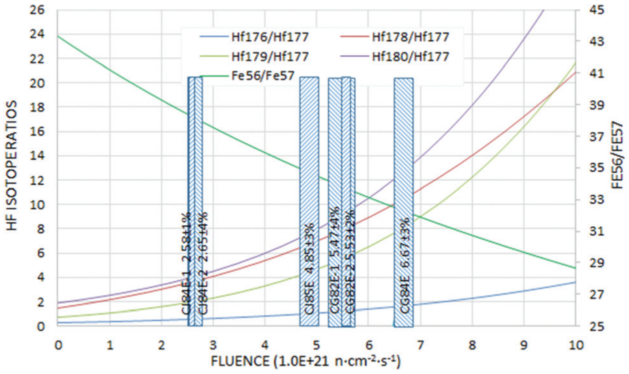

Fig. 5 Neutron fluence estimation using IRM

Inductively coupled plasma-mass spectrometry analysis of ^{56}Fe and ^{57}Fe can be problematic due to interference from very high signals from the plasma ion species, ^{40}Ar^{16}O^{+} and ^{40}Ar^{16}OH^{+}. A high-resolution ICP-MS was used to resolve the Fe isotope peaks from the plasma ion peaks, which resulted in a reduced sensitivity in determining the ^{56}Fe/^{57}Fe ratio. This ratio was determined with greater uncertainty than hafnium isotope ratios due to the high background caused by plasma ion species and reduced sensitivity using the higher resolution settings.

Mass spectrometric determination of isotope ratios relies on standardization of reference materials with known isotope ratios. In this paper, single-element standard solutions of iron and hafnium with natural isotope abundances were used, and their generally accepted values, isotope ratios and uncertainties [12] proved to be more than adequate as isotope references.

To meet the radio activity requirement of the ICP-MS lab, one sample of approximately 10 mg was taken from each irradiated Zr-2.5Nb specimen in a CNL hot cell facility. Samples were weighed and dissolved with 1 mL of nitric acid and 0.5 mL of hydrofluoric acid (Optima grade, Fisher Scientific) and made to 20 mL solution first and then further diluted ten times for ICP-MS analysis. The Zr-Nb matrix concentration was kept near 50 $\mu g \cdot mL^{-1}$ so that it did not affect the analysis of the selected hafnium and iron isotopes. The uncertainty (95% confidence interval) for isotope ratio measurement was estimated to be ±3% for hafnium isotope ratios and ±6% for that of ^{56}Fe/^{57}Fe.

2.4 IRM Results and Discussion. The estimates of neutron fluence using IRM are illustrated in Fig. 5. The neutron fluence values were obtained by taking the average of the fluence values indicated by four hafnium and one iron isotope ratios.

Table 5 compares the neutron fluence values, which were estimated using IRM, with the measured values. The uncertainties in the IRM estimates were approximated using one standard deviation of their predicted values. The maximum uncertainty of the six samples shown in Table 5 is ±4%. The IRM-estimated and the measured neutron fluence values agree within ±3% for all the samples except for CG84E. The discrepancies, in general, result from the uncertainties associated with predictions using WIMS/TRIAD, irradiation conditions (including irradiation history and sample location) in NRU, and ICP-MS measurements. The

Table 4 Natural abundances (%) of stable isotopes and half-lives of radionuclides of interest

Mass	54	56	57	58	Mass	174	176	177	178	179	180
Cr	2.365				Yb	31.8	12.7				
Mn	312 d				Lu	3.31 y	2.59	6.65 d		4.59 h	
Fe	5.845	91.754	2.119	0.282	Hf	0.16	5.21	18.6	27.3	13.6	35.1
Co		77 d	271 d	71 d	Ta			56.6 h		1.82 y	0.01
Ni		6 d	35 h	68.08	W				21.6 d		0.13

Table 5 Neutron fluence in Zr-2.5Nb damage monitor samples (1.0×10^{21} n cm^{-2})

Sample ID	Measured	IRM ± s[a]	$\left(\frac{\text{IRM estimated}}{\text{measured}} - 1\right)$
CG84E	7.46	6.67 ± 3%	−11%
CJ85E	4.71	4.85 ± 3%	3%
CG82E-1	5.38	5.47 ± 4%	2%
CG82E-2	5.38	5.53 ± 2%	3%
CJ84E-1	2.63	2.58 ± 1%	−2%
CJ84E-2	2.63	2.65 ± 4%	1%

[a] s is defined as $\sqrt{\frac{\sum (x-\bar{x})^2}{n-1}}$, where $\bar{x}$ is the sample mean, average (x^1, x^2,…), and n is the sample size.

correlations presented in Sec. 2.2 between indicator isotope ratios and neutron fluence confirm that there is no change in phenomenon within the sample fluence range. The larger discrepancy in CG84E compared to that of other samples may be caused by uncertainty related to its irradiation condition, in particular, sample location.

3 Conclusion

This paper describes the results of a study in which the IRM was used to estimate the neutron fluence of Zr-2.5Nb materials irradiated in the NRU fast neutron irradiation facilities. The results are summarized below:

- Hafnium and iron have been shown to be good indicators for neutron fluence, and they are commonly found in Zr-2.5Nb material.
- ICP-MS can measure the indicator element isotope ratios with an uncertainty of less than ±4%, using material specimens weighing as little as 10 mg.
- IRM is able to estimate the neutron fluence in Zr-2.5Nb materials within ±11% of measured values.

This study shows that IRM is able to estimate neutron fluence with low uncertainty in Zr-2.5Nb materials irradiated in NRU without requiring irradiation histories or in-core measurements. This provides a great benefit for studies of irradiation effects on materials.

Given that NRU is a heavy-water moderated reactor design, it may be feasible to apply this method to estimate neutron fluence in critical reactor components such as pressure and calandria tubes in CANDU reactors. A next logical step is to qualify this method for materials irradiated in CANDU reactors with CANDU-specific data and specimens.

Applying IRM to estimate neutron fluence in CANDU reactors would lead to improved understanding of the effects of irradiation damage on those critical reactor components and to assess the changes to their predicted service life.

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