Analysis of New Measurements of Calvert Cliffs Spent Fuel Samples Using SCALE 6.2*

J. Hu, J.M. Giaquinto, I.C. Gauld, G. Ilas, and T.J. Keever
Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831-6172, United States
huj1@ornl.gov

Abstract

High quality experimental data for isotopic compositions in irradiated fuel are important to spent fuel applications, including nuclear safeguards, spent fuel storage, transportation, and final disposal. The importance of these data has been increasingly recognized in recent years, particularly as countries like Finland and Sweden plan to open the world's first two spent fuel geological repositories in 2020s, while other countries, including the United States, are considering extended dry fuel storage options. Destructive and nondestructive measurements of a spent fuel rod segment from a Combustion Engineering 14 × 14 fuel assembly of the Calvert Cliffs Unit 1 nuclear reactor have been recently performed at Oak Ridge National Laboratory (ORNL). These ORNL measurements included two samples selected from adjacent axial locations of a fuel rod with initial enrichment of 3.038 wt% ²³⁵U, which achieved burnups close to 43.5 GWd/MTU. More than 50 different isotopes of 16 elements were measured using high precision measurement methods. Various investigations have assessed the quality of the new ORNL measurement data, including comparison to previous measurements and to calculation results. Previous measurement data for samples from the same fuel rod measured at ORNL are available from experiments performed at Pacific Northwest National Laboratory in the United States and the Khoplin Radium Institute in Russia. Detailed assembly models were developed using the newly released SCALE 6.2 code package to simulate depletion and decay of the measured fuel samples. Results from this work show that the new ORNL measurements provide a good quality radiochemical assay data set for spent fuel with relatively high burnup and long cooling time, and they can serve as good benchmark data for nuclear burnup code validation and spent fuel studies.

Keywords: destructive assay, radiochemical analysis, spent fuel, isotopic composition, burnup, validation, Calvert Cliffs, SCALE

1. Introduction

High quality experimental data for isotope compositions in irradiated fuel are important to spent fuel applications, including interim and long-term storage, transportation, and final disposal. The importance of these data has been increasingly recognized as countries like Finland and Sweden plan to open the world's first two spent fuel geological repositories in the next decade, and other countries, including the United States, are considering extended dry fuel storage options. The isotope compositions in spent fuel define the fuel's characteristics, such as residual decay heat and radioactivity. Quantification of uncertainties in isotope compositions is important since these uncertainties can directly impact safety margins of a given spent fuel facility. Destructive assay (DA), also known as radiochemical assay (RCA), is the gold standard method to measure spent fuel isotope compositions; nondestructive assay (NDA) techniques only measure a limited number of observables (mainly neutron and gamma radiations). Therefore, NDA techniques cannot be directly used to quantify all isotopes important to spent fuel applications. DA is a complex procedure that includes cutting fuel samples, dissolving the fuel, dilution, sample preparation, chemical separation, and mass spectrometry. For high precision measurements, the solution must be spiked using known enriched isotopic standards. Errors in any of the measurement steps can lead to errors in measurement results that would be difficult to identify. Therefore, it is important to verify the quality of the measurement data before they can be used for safety purposes.

In this work, two fuel-pellet scale spent fuel samples from the same fuel rod were used, which was extracted from a fuel assembly that had been irradiated in the Calvert Cliffs Unit 1 (CC-1) pressurized water reactor (PWR). The samples were measured using DA at Oak Ridge National Laboratory (ORNL) between 2010 and 2011. A large selection of isotopes (51) was considered in this experiment. A similar DA measurement campaign was recently performed at ORNL on 5 spent fuel samples from the Three Mile Island-1 reactor; these measurements were analyzed using SCALE 6.1.3 and documented [1]. In addition to DA for the two CC-1 samples, gamma spectrometry was performed on the fuel rod segment from which these samples were obtained. Computer models were developed to simulate the burnup and decay of the measured spent fuel samples using the latest release of SCALE in 2016, version 6.2 [2]. The new CC-1 experimental data provides an additional benchmark to validate SCALE 6.2 and compare the accuracy of this new version to version 6.1.3.

*This manuscript has been authored by UT-Battelle, LLC, under Contract No. DE-AC0500OR22725 with the U.S. Department of Energy. The United States Government retains and the publisher, by accepting the article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for the United States Government purposes. The Department of Energy will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan (<http://energy.gov/downloads/doe-public-access-plan>).

Under the Approved Testing Material (ATM) program sponsored by the US Department of Energy (DOE) Office of Civilian Radioactive Waste Management (OCRWM), studies on spent fuel were conducted in the 1980s to 1990s to investigate fuel and cladding characteristics, radioisotope inventory, and redistribution of fission products [3]. Under the ATM program, CC-1 fuel samples (ATM-104) from the same fuel rod measured at ORNL were previously measured at Pacific Northwest National Laboratory (PNNL) in the US and at Kholin Radium Institute (KRI) in Russia in 1987 and 1995, respectively [4]. Those measurement data served as a benchmark for validating irradiated fuel data used in criticality calculations and were used for the Organisation for Economic Co-operation and Development/Nuclear Energy Agency burnup credit criticality safety calculation benchmark [5]. Those independent measurements also provide an important benchmark to cross-check and evaluate the new ORNL measurement data. Compared to the previous measurements, the ORNL measurements included a few more isotopes (e.g., ^{244}Cm). More rigorous treatments for the lanthanides were taken in the ORNL measurements, including incorporation of isotope dilution techniques and high pressure separations for faster and more efficient separations, which resulted in cleaner element fractions. In addition, these measurements used isotope dilution for a larger suite of elements than the previous measurements.

2. Description of the Measured Fuel Samples

The CC-1 reactor is a PWR with a generating capacity of 900 MWe operated in the US since 1975. Under the ATM -104 spent fuel program, three CC-1 assemblies were analyzed at PNNL [3]. Examinations conducted on the fuel included gamma scanning, fission gas analyses, ceramography, metallography of the cladding, electron probe microanalyses, analytical transmission electron microscopy, fuel burnup measurements, and radiochemical analyses of the fuel and cladding [3]. DA measurements were performed for nine fuel samples taken from three different fuel rods, with one rod from each of the three considered assemblies. For the work described in this paper, three samples from rod MKP109 of assembly D047 are of particular interest because the two samples measured at ORNL were also taken from this fuel rod.

Assembly D047 is a Combustion Engineering (CE) 14×14 design with 176 fuel rods and 5 large guide tubes for the assembly control cluster. Fig. 1 shows the schematic of the assembly design with 7 intermediate grid spacers, as well as one at the bottom and another at the top. The assembly layout illustrated in Fig. 2 highlights the location of rod MKP109. The guide tubes are much larger than those of other PWR assembly types, with each guide tube occupying the space of four fuel rods. Fig. 3 shows the fuel rod and pellet dimensions of assembly D047. The length of the measured rod is 373 cm, and the active fuel length is 347.2 cm. Table 1 summarizes the assembly design and operating data [4] for the reactor and assembly D047. The initial enrichment of the UO_2 fuel in rod MKP109 was 3.038 wt% ^{235}U . No burnable poison or control rods were used in this assembly during its irradiation in the reactor.

Fig. 1. Schematic of Combustion Engineering 14×14 fuel assembly (Ref. [3], Fig. 3.1).

Fig. 2. Configuration of assembly D047 from CC-1 (Ref. [3], Fig. 3.3).

Fig. 3. Fuel rod and pellet dimensions of assembly D047 (Ref. [3], Fig. 3.2).

Table 1. Design and operating data for assembly D047 [4].

Assembly and reactor data	Value
Operating pressure, MPa	15.5
Core coolant inlet temperature, K	557
Core coolant outlet temperature, K	585
Lattice geometry	14 × 14
Number of fuel rods	176
Number of guide tubes	5
Number of burnable poison rods	0
Assembly pitch, cm	20.78
Total fuel rod length, cm	373
Active fuel rod length, cm	347
Fuel rod data	
Fuel material type	UO ₂
Pellet stack density, g/cm ³	10.045
Fuel pellet diameter, cm	0.9563
Clad material	Zircaloy-4
Clad inner diameter, cm	0.9855
Clad outer diameter, cm	1.1176
Average clad temperature, K	620
²³⁵ U enrichment, wt%	3.038
Guide tube data	
Guide tube material	Zircaloy-4
Inner radius, cm	1.314
Outer radius, cm	1.416

Fig. 4 illustrates the cycle history of assembly D047. This assembly was irradiated for four consecutive cycles, from cycle 2 to cycle 5, between 1977 and 1982. Except for a period of about 5 months at reduced power during cycle 4 and a short down time for cycle 3, the reactor operated at essentially full power during the four cycles. The average final burnup for the assembly is 41.8 GWd/MTU. The day-to-day power variation was not modeled in this work; instead, cycle average power was used, which was considered appropriate given the last cycle (cycle 5) of this assembly was irradiated at nearly full power. The in-core location or shuffling of this assembly in each cycle is shown in Figure 3.4 of Ref. [3]. Assembly shuffling was not simulated in the current model, as the analyzed samples were taken from interior fuel rods; the impacts of neighboring assemblies on the isotope contents in such rods were previously shown to be small [6].

Fig. 4. Cycle history of assembly D047 and the reactor (Ref. [3], Fig. 3.5).

For assembly D047, rod MKP109 is the only fuel rod measured using DA. As mentioned above, three samples designated as LL, CC, and P were cut from this rod; these had been measured at PNNL in 1987. However, PNNL's measurement of lanthanide isotopes in those three samples did not separate out individual elements, so calculations were required to infer individual quantities for the isotopes of different elements but with the same atomic mass. The lanthanide measurements were performed again at KRI in 1995. KRI's measurements of Sm, Eu, and Gd isotopes and PNNL's measurements of the non-lanthanide isotopes were adopted in a previous study for code validation [5] and were also used in this work for comparison purposes.

A segment of rod MKP109, designated as Segment G (approximately 8 inches long), was shipped from Argonne National Laboratory to ORNL in 2009. Two samples, designated here as S1 and S2, were cut from this segment and measured at ORNL. Table 2 shows detailed information about the five measured samples, including sample burnup, axial location along the fuel rod, cooling time, moderator density and temperature, and fuel temperature [4]. These samples have similar nominal lengths of 2–3 cm. Samples P, S1, and S2 have similar burnups because they were all taken from the central region of Rod MKP109, where the axial burnup profile is relatively flat; therefore, Measurement of Sample P was re-analyzed in this work to cross check the recent ORNL measurements. Samples S1 and S2 were taken from two adjacent rod locations. Because these samples were taken from different heights on the fuel rod, special care was applied in the computational model to account for the variations of moderator and fuel conditions with the sample axial location. Though only time-integrated values are shown in Table 2 for fuel temperatures, time-varying values were used in the computational models. As expected, the fuel and moderator temperatures increase, whereas the moderator density decreases along the height of the fuel rod. Table 3 shows the average boron concentration, the average irradiation power on Sample S1 and S2, and the irradiation duration time in each cycle. Time-varying boron concentration was modeled in this work, although only cycle average boron is shown in this table. The irradiation power was scaled based on reported burnup of this assembly in each cycle.

Table 2. Summary of samples from rod MKP109.

Sample ID	Axial location ^a (cm)	Burnup ^b (GWd/MTU)	Cooling time ^c (year)	Moderator temperature (K)	Moderator density (g/cm ³)	Fuel temperature ^d (K)
104-MKP109-LL [4]	360.7	27.35	5.12, 11.43	557	0.7575	784
104-MKP109-CC [4]	346.0	37.12	5.12, 12.76 ^e	558	0.7569	829
104-MKP109-P [4]	209.3	44.13	5.12, 12.76	570	0.7307	840
ORNL-S1	94.0	43.50	28.69 ^f	583	0.7059	847
ORNL-S2	92.0	43.45	28.69	583	0.7059	847

^a measured from the top of the fuel rod

^b measured using ¹⁴⁸Nd

^c time since the fuel was discharged from reactor when the samples were measured in DA

^d life-time average effective temperature shown here, although cycle-dependent temperature was modeled

^e 5.1 corresponds to the PNNL measurement and 12.7 corresponds to the KRI measurement on lanthanides

^f the average value; the measurements span through 2010 to 2011; exact days were modelled in this work

Table 3. Burnup history data for samples S1 and S2

Cycle #	Average boron ^a (ppm)	Average power ^b (MW/MTU)	Duration (days)
2	557	34.21	306
3	558	29.69	382
4	570	24.61	466
5	583	22.28	461

^a The concentration of soluble boron in moderator varies day-to-day; here is the time-integrated boron concentration in each cycle.

^b average irradiation power on Sample S1 and S2 based on measured burnups

4. Measurements

4.1 Gamma scan

Axial gamma scans were performed on the entire fuel rod MKP109 at PNNL in 1987. Gamma scans were also performed for rod segment G at ORNL in 2009. The gamma scan of segment G and the cutting of ORNL samples were documented in an ORNL scientific notebook [7]. The gamma scan used the ¹³⁷Cs peak to determine the burnup profile, ensure no anomalies in the burnup distribution at the region of the samples, confirm the orientations of the rod segments after shipping, and locate fuel pellet interfaces for purposes of cutting samples. Note that these gamma scans were not used for quantitative analysis in this work because the exact experiment setups were unknown to the authors.

Fig. 5 shows the axial gamma scan [3] of Rod MKP109, including the locations of the three PNNL samples (P, CC, and LL) and the two new ORNL samples (S1 and S2). As shown, the fuel rod has a flat axial burnup in the center region of the rod. Samples CC and LL are located near the bottom of the fuel, whereas samples S2, S1, and P are all located in the flat burnup region. Depressions of ¹³⁷Cs activity at the assembly's seven grid spacer locations are clearly shown. The grid spacers displace water and reduce thermal neutron flux in their proximity, causing power (and burnup) to decrease in their vicinity.

Fig. 6 shows a detailed plot of the gamma scan on segment G of rod MKP109. The peaks in the scan indicate the location of fuel pellets and the dips occurring at the pellet interfaces. The cut locations, indicated by the dashed lines in the figure, were made at the center of the pellets. Each ORNL sample contained two half pellets and one full pellet, with a total fuel sample length of ~ 2.2 cm. This procedure ensured that a sufficient amount of fuel material was available for representative measurements, and it minimized effects that may be present due to fuel inhomogeneity and fission product migration. Sample S1 is ~6 cm away from the closest grid spacer, and sample S2 is ~8 cm away. The burnup of S1 seems to be slightly affected by the grid spacer.

Fig. 5. Axial ^{137}Cs gamma scans of rod MKP109; locations and types of radiochemical samples from rod MKP109 (Ref. [3], Figure 4.2).

Fig. 6. Axial ^{137}Cs gamma scans on segment G (of rod MKP109), from which the two ORNL samples (S1 and S2) were cut; the dashed cutting lines also shown [7].

4.2. Destructive analysis

4.2.1. Experimental techniques and measured isotopes

The experimental techniques, isotopes measured by each technique, and associated uncertainties for measurements of the two ORNL samples are listed in Table 4. For the uncertainties, the relative standard deviations (RSD) of one sigma are included in parenthesis for each isotope and technique. The isotopes shown in this table are widely considered in many modern experimental programs [8] [9] because of their importance to a broad range of applications including burnup credit, radiological safety and radiation sources, and nuclear decay heat. Many of these isotopes were not measured by DA in earlier programs. ^{243}Am , ^{140}Ce , ^{142}Ce , ^{244}Cm , ^{152}Gd , ^{157}Gd , ^{139}La , ^{95}Mo , and ^{101}Ru were not measured by PNNL or KRI [4] [5], while ^{134}Cs and ^{99}Tc , which were previously measured by PNNL, were not measured by ORNL. As shown, isotope dilution mass spectrometry (IDMS) has the lowest uncertainties among these techniques, and IDMS was used for the measurement of 40 isotopes in this work, which was about twice as many as the PNNL and KRI measurements [4]. As experimental results were reported in different units (e.g., Ci/g fuel, g/g fuel, and %atom), unit conversions were performed to enable consistent comparisons.

Table 4. Experimental techniques, measured isotopes, and uncertainties in the ORNL measurements

Experimental technique	Isotope(% relative standard deviation)
Gamma spectrometry	$^{137}\text{Cs}(5)$, $^{154}\text{Eu}(5)$, $^{241}\text{Am}(5)$
Alpha spectrometry	$^{238}\text{Pu}(5)$, $^{243}\text{Am}(5)$, $^{241}\text{Am}(5)$, $^{244}\text{Cm}(5)$
Beta spectrometry	$^{90}\text{Sr}(5)$
ICPMS ^a with external calibration	$^{139}\text{La}(5)$, $^{95}\text{Mo}(5)$, $^{101}\text{Ru}(5)$, $^{103}\text{Rh}(5)$, $^{237}\text{Np}(5)$, $^{243}\text{Am}(5)$, $^{244}\text{Cm}(5)$
IDMS ^b	^{133}Cs , ^{135}Cs , ^{137}Cs (1) ^c ; ^{140}Ce , ^{142}Ce (1); ^{143}Nd , ^{144}Nd , ^{145}Nd , ^{146}Nd , ^{148}Nd , ^{150}Nd (1), ^{142}Nd (1.4); ^{147}Sm , ^{148}Sm , ^{150}Sm , ^{152}Sm , ^{154}Sm (1), ^{149}Sm , ^{151}Sm (2.7); ^{151}Eu , ^{154}Eu (2.1), ^{152}Eu , ^{155}Eu (15), ^{153}Eu (1); ^{152}Gd , ^{157}Gd (15), ^{154}Gd , ^{155}Gd , ^{156}Gd , ^{158}Gd (1), ^{160}Gd (2.7); ^{234}U (5), ^{235}U , ^{236}U (1.4), ^{238}U (1); ^{241}Pu , ^{242}Pu (1.4), ^{239}Pu , ^{240}Pu (1)

^a ICPMS = inductively coupled plasma mass spectrometry

^b IDMS = isotope dilution mass spectrometry (ICPMS with spiking using known enriched isotopic standards)

^c ^{133}Cs , ^{135}Cs , and ^{137}Cs all had 1% relative standard deviation

4.2.2 Dissolution methods

Dissolution of the spent fuel samples for DA were performed within a shielded hot cell cubicle using a digestion rig specifically designed for high precision recovery and quantification of the elements and isotopes analyzed. More details about the dissolution procedures can be found in Ref. [1]. The weight of the fuel was calculated as the difference between the initial total fuel-clad weight and the post-digestion cladding weight. Details of the sample preparation for DA and of the weight measurements can be found in Ref. [1]. For this set of fuel digestions, analysis of the undissolved solids (UDS) was not performed. However, for past spent fuel digestions using the same procedure, detailed analysis of the UDS metallics showed minimal concentrations of elements of interest [10].

4.2.3 Actinides and fission products measured by gamma spectrometry and alpha spectrometry

As shown in Table 4, some isotopes are measured by gamma spectrometry and some by alpha spectrometry. For gamma spectrometry measurements, digested spent fuel aliquots were diluted using nitric acid to obtain a count rate with <10% dead time. A Canberra Genie-2000 Data Acquisition System, in conjunction with high purity germanium detectors and Canberra Lynx modules, were used for measurement and data reductions. The systems were calibrated using National Institute of Standards and Technology (NIST) traceable QCY48 mixed gamma isotope standards. Daily calibration verifications were measured using secondary NIST traceable standards.

For alpha spectrometry, aliquots were diluted using nitric acid to obtain a satisfactory gross count rate and to keep the amount of solids on a plate to a minimum. Same alpha spectrometry measurement procedures were followed as the ones used for the TMI-1 fuel [1]. The alpha spectrometry analyses were used to determine emitted alpha energy ratios and were used in conjunction with the respective gross alpha analysis to associate alpha activity to the detected alpha energies.

4.2.4 Actinides and fission products measured by ICPMS external calibration

Selected actinide and fission product isotopes were measured using inductively coupled plasma mass spectrometry (ICPMS) with external calibration. External calibration curves for each of the fission product isotopes were made using NIST traceable certified standards. Same measurement procedures were followed as the ones used for the TMI-1 fuel [1].

4.2.5 Actinide and fission products HPLC separations for IDMS

Selected actinide and fission product isotopes were measured using isotope dilution mass spectrometry (IDMS), which is essentially ICPMS with spiking using known enriched isotopic standards. In this work, the same IDMS measurement procedures and enriched spiking standards were used as in the measurement of the TMI-1 fuel, and the details can be found in Ref. [1]. For the lanthanides, the high-performance liquid chromatography (HPLC) separation process involved loading the samples onto the

analytical column in high nitric acid. Next, complexation of the uranium using dilute hydrochloric acid removed the bulk of the fuel matrix to waste. Lastly, the trace lanthanide elements were selectively eluted off the column by chelation chromatography using a dilute solution of 2-hydroxyisobutyric acid (HIBA). This analytical methodology effectively isolates purified fractions of each lanthanide element from the high uranium matrix of the dissolver solution for high accuracy isotopic measurements. The purified fractions were measured for their respective element's isotopic abundances using quadrupole ICPMS.

4.2.6. Isotopic ratio measurements of purified fractions by IDMS

Isotope ratio measurements were performed using an X-SeriesII (Thermo-Scientific, Franklin, MA) quadrupole ICPMS. For sample introduction, an APEX-HR desolvating inlet system coupled to a Spiro TMD (heated Teflon® Membrane Desolvator, Elemental Scientific Inc., Omaha, NE) was used. This introduction system reduces solvent oxide, hydride, and carbide polyatomic interferences while optimizing signal sensitivity and stability. The system was further optimized for signal response and stability by monitoring oxide levels, mass response, and detector dead-time determinations via a tuning solution designed for this optimization process. Typical short-term stability for the major isotopes monitored during tuning was < 1% relative standard deviation. Oxides were < 0.03%.

Measurement for mass discrimination for the lanthanide elements were obtained by using commercially available NIST traceable natural-abundant single-element standards. For caesium, a natural barium standard was used. International Union of Pure and Applied Chemistry (IUPAC) isotopic abundances were used in comparison to the measured ratios to calculate the mass bias for each ratio measured. For uranium, the mass bias standard used was NLB CRM 117, and for plutonium, CRM 137 was used.

4.2.7. Burnup analysis

The burnup for each CC-1 sample was determined experimentally using the guidance established in ASTM E 321-96, *Standard Test Method for Atom Percent Fission in Uranium and Plutonium Fuel (Neodymium-148 Method)* [11]. The overall effective fractional fission yield for Nd-148 was determined to be 0.01706 using the fission yields of ²³⁵U, ²³⁹Pu, ²⁴¹Pu, and ²³⁸U weighted by the percent fission per the guidance in the ASTM standard method. With the measured ¹⁴⁸Nd and actinide concentrations, % fission per initial metal atom (%FIMA) is determined using this standard method. To convert %FIMA to more commonly used burnup units of GWd/MTU, an approximate conversion factor of 9.6+/-0.3 (GWd/MTU/%) can be used [11]. Alternatively, the burnup can also be determined using burnup codes by varying the burnup until the calculated ¹⁴⁸Nd concentration or other fission indicators match the measured value.

Table 5 shows the burnup values of Samples S1 and S2 determined using these two methods based on the measured ¹⁴⁸Nd quantities. The uncertainty as calculated using SCALE includes only the uncertainty in the measured ¹⁴⁸Nd concentration. As shown, SCALE yields results similar to the ASTM standard method.

Table 5. Burnup estimations for ORNL samples (S1 and S2)

	Sample S1	Sample S2
% FIMA	4.53 ± 0.068	4.53 ± 0.068
GWd/MTU, ASTM ¹⁴⁸ Nd method	43.50 ± 0.653	43.45 ± 0.652
GWd/MTU, SCALE	43.62 ± 0.654	43.47 ± 0.652
% Relative difference (SCALE vs. ASTM method)	0.29 ± 0.004	0.05 ± 0.001

4.2.8. Uncertainties

Evaluations of the combined standard uncertainties (CSUS) for IDMS results were performed with the use of GUM Workbench software, version 2.4 [12]. GUM Workbench incorporates the principles set forth in the ISO/IEC document titled "Guide to the Expression of Uncertainty in Measurement," and it provides a systematic way to capture the uncertainties associated with each step of an analytical methodology.

The measurement uncertainties of each isotope for a given technique are shown in Table 4. For isotopes that were measured using beta counting, gamma, alpha spectrometry, or external calibration mass spectrometry, the RSD is about 5% based on historical trends for measurement of controlled samples.

The uncertainty (RSD) for most isotopes measured using IDMS is 0.5%. However, for isotopes with relatively low abundance compared to other isomers, the uncertainties are higher. This is attributed to precision limits of the ICPMS mass spectrometer measurements. For the isotopes that were measured using multiple methods, discrepancies in measured (or inferred) isotope masses among different methods were identified. For example, the measured ¹³⁷Cs and ¹⁵⁴Eu masses in these two samples by IDMS differ by 2–9% from the mass values inferred by gamma spectrometry, and the measured ²⁴³Am masses inferred by alpha spectrometry were 1.4–2.8 times that of those measured by IDMS. The mass values were also compared to calculations, and it was found that the IDMS values had closest agreements to calculations; thus, the IDMS values (when available for a given isotope) were adopted in this work.

4.2.9. Adjustment for mass imbalance

A global check on the measured concentrations was first performed using a mass balance calculation that compares the heavy metal mass of the fuel sample prior to dissolution, obtained by weighing, against the measured heavy metal mass (total masses of the measured actinides in the samples) in the solution corrected for losses due to fission (other types of reactions do not reduce the heavy metal quantities). The number of fissions was obtained from the measured values of %FIMA in Table 5. The

mass converted to energy during the fission process was negligible and was thus not considered in this calculation. The measured heavy metal mass (after correction for loss to fission) was found to be 2.2–2.4% greater than that inferred from sample weight, which was likely due to handling of sample solutions. Such mass imbalance was found to be less than 1% [1], except for one sample that had 1.6%, in the TMI-1 measurements, and up to 4% in other programs [13]. To account for the imbalance, the as-delivered isotope concentration results were re-normalized based on the measured heavy metal mass (after correction for loss to fission).

5. Computational analysis

5.1. Codes and nuclear data

SCALE is widely used internationally by industry, regulatory authorities, safeguards agencies, and research institutions for nuclear systems design and spent nuclear fuel studies. The depletion and decay methods are based on the Oak Ridge Isotope Generation (ORIGEN) code [14] in SCALE, and they have been extensively validated using DA data for more than 150 samples from commercial light water reactors [14] [15].

A study summarizing SCALE validation for spent fuel calculations [15], which employed SCALE 6.1 with ENDF/B-VII.0 cross section data, was used as a reference in this work. For a set of isotopes important to various spent fuel applications, the study provided mean relative differences between SCALE-calculated isotope concentrations and corresponding experimental values, averaged over measurements of dozens of PWR spent fuel samples, as well as the corresponding standard deviations. That set of data is referred to as *historical data* herein.

Accurate cross sections are required for depletion codes to simulate transmutation of the fuel during depletion. Within SCALE, time-dependent cross sections for depletion may be calculated using either one-dimensional (XSDRN S_N code), two-dimensional (2-D) (NEWT S_N code), or three-dimensional neutron transport (KENO Monte Carlo code) capabilities. The transport code may be selected by the user based on the geometric complexity of the problem to be solved. SCALE couples the transport analysis for the fuel assembly model with the ORIGEN code that calculates the time-dependent isotope compositions during irradiation and decay, and generates radiological properties of the fuel such as decay heat and neutron and gamma-ray emission rates and energy spectra. The depletion calculation is performed within an automated SCALE sequence called TRITON [16], which performs all data handling and execution of all the codes required for the complete time-dependent analysis. In this study, NEWT was chosen to perform the transport calculations with TRITON.

The recently released SCALE 6.2 package provides several new capabilities and improvements [2]. Below are several examples relevant to the depletion capabilities in SCALE/TRITON:

- Compared to previous SCALE versions, substantial speedups (generally 4×) in depletion calculations are realized with TRITON (using NEWT) due to optimizations within the NEWT code.
- New 252-group cross section data are introduced in SCALE 6.2, improving agreement between multigroup and continuous-energy calculations using a more detailed representation of the ^{238}U resonance structure in low enrichment uranium light water reactor systems.
- The ORIGEN code has been modernized and includes a new high-performance solver.
- ENDF/B-VII.1 nuclear data libraries are introduced in SCALE 6.2

The ENDF/B-VII.1 252-group cross section library was used in this study. The measurement data analyzed in this work provides an additional benchmark to validate SCALE 6.2 and compare results with the previous version of SCALE.

5.2. Assembly model

The irradiation of assembly D047 was simulated using the TRITON model illustrated in Fig. 7. The model was developed using the geometry and material data listed in Table 1, moderator and fuel conditions listed in Table 2, and power data for each cycle as provided in Fig. 4. The detailed time-dependent soluble boron concentration in the coolant and the fuel temperature during irradiation were included in the model. Burnup steps (one transport calculation per step) corresponding to ~2 GWd/MTU were used in this calculation. Only half of the assembly geometry was modeled using symmetry. This 2-D model effectively represents a cross section of the actual assembly (slice) at the elevation of the measured sample. The measured rod MKP109 and its four immediate neighboring fuel rods were individually depleted (individual depletion mixtures were used, as indicated by different colors in Fig. 7), whereas the rest of the fuel rods in the assembly were modeled as a single depletion mixture. Prior study has demonstrated that this simplification has marginal impacts on calculated concentrations of the isotopes considered in this work for the rod under study while it dramatically improves modeling efficiency [4].

Fig. 7. Model of upper half of assembly D047.

6. Results and discussion

6.1. Measured concentrations in samples S1 and S2

Table 6 shows the measured isotope concentrations in the ORNL Samples S1 and S2, the associated measurement uncertainties, and a comparison of the two samples. The measured concentrations are in unit of g/g fuel. Because both samples were taken from adjacent fuel rod segments, they are expected to contain similar quantities of each isotope. Therefore, the ratio of concentration for each isotope in Sample S1 to that in S2 is used as a consistency check. As shown in this table, the relative differences between these two samples are small for the majority of the isotopes, but there are a few exceptions, as highlighted with gray background in the table, for which the relative difference is at least three times larger than the measurement RSD: ^{151}Eu , ^{152}Eu , ^{152}Gd , ^{157}Gd , ^{160}Gd , ^{240}Pu , ^{241}Pu , and ^{242}Pu . Note that ^{238}Pu were measured in two different ways as explained in the footnotes to the table; however, the values measured by the “Alpha spectrometry + IDMS” were adopted for further analysis in this work because of their higher precision.

Table 6. Measured isotope concentrations in Sample S1 and S2.

Isotope	Measurement method	Measurement date (mm/dd/yy)	Measured concentration (g/g fuel)		Measurement RSD ^a (%)	Rel. diff. ^b (%)
			Sample S1	Sample S2		
^{241}Am	Gamma spectroscopy	09/17/10	8.47E-04	9.24E-04	5.0	9.1
^{243}Am	ICPMS ^c	10/21/10	1.69E-04	1.75E-04	5.0	3.6
^{140}Ce	IDMS	02/07/11	1.36E-03	1.35E-03	1.0	-0.7
^{142}Ce	IDMS	02/07/11	1.23E-03	1.21E-03	1.0	-1.6
^{244}Cm	ICPMS	10/21/10	2.88E-05	2.99E-05	5.0	3.8
^{133}Cs	IDMS	05/25/11	1.20E-03	1.19E-03	1.0	-0.8
^{135}Cs	IDMS	05/25/11	4.19E-04	4.17E-04	1.0	-0.5
^{137}Cs	IDMS	05/25/11	6.70E-04	6.67E-04	1.0	-0.4
^{151}Eu	IDMS	02/07/11	2.76E-06	2.26E-06	2.7	-18.1
^{152}Eu	IDMS	02/07/11	2.64E-08	1.50E-07	15.0	468.2
^{153}Eu	IDMS	02/07/11	1.32E-04	1.32E-04	1.0	0.0
^{154}Eu	IDMS	02/07/11	2.58E-06	2.51E-06	2.7	-2.7
^{155}Eu	IDMS	02/07/11	1.47E-07	1.63E-07	15.0	10.9
^{152}Gd	IDMS	02/23/11	4.92E-08	1.09E-07	15.0	121.5
^{154}Gd	IDMS	02/23/11	2.89E-05	2.88E-05	1.0	-0.3
^{155}Gd	IDMS	02/23/11	1.02E-05	1.01E-05	1.0	-1.0
^{156}Gd	IDMS	02/23/11	1.42E-04	1.43E-04	1.0	0.7
^{157}Gd	IDMS	02/23/11	3.55E-07	2.04E-07	15.0	-42.5
^{158}Gd	IDMS	02/23/11	2.25E-05	2.21E-05	1.0	-1.8
^{160}Gd	IDMS	02/23/11	1.78E-06	1.55E-06	2.7	-12.9
^{139}La	ICPMS	10/21/10	1.45E-03	1.52E-03	5.0	4.8
^{95}Mo	ICPMS	10/21/10	8.35E-04	8.14E-04	5.0	-2.5
^{142}Nd	IDMS	02/07/11	3.14E-05	3.24E-05	1.4	3.2
^{143}Nd	IDMS	02/07/11	7.81E-04	7.82E-04	1.0	0.1
^{144}Nd	IDMS	02/07/11	1.63E-03	1.62E-03	1.0	-0.6
^{145}Nd	IDMS	02/07/11	7.30E-04	7.31E-04	1.0	0.1
^{146}Nd	IDMS	02/07/11	8.21E-04	8.21E-04	1.0	0.0
^{148}Nd	IDMS	02/07/11	4.28E-04	4.26E-04	1.0	-0.5
^{150}Nd	IDMS	02/07/11	2.07E-04	2.06E-04	1.0	-0.5
^{237}Np	ICPMS	10/21/10	5.09E-04	5.40E-04	5.0	6.1
^{238}Pu	Alpha spectrometry with absolute calibration ^d	09/17/10	2.59E-04	2.24E-04	5.0	-13.3

²³⁸ Pu	Alpha spectrometry + IDMS ^c	05/18/11	1.94E-04	2.11E-04	1.0	8.5
²³⁹ Pu	IDMS	05/18/11	4.36E-03	4.57E-03	1.0	4.9
²⁴⁰ Pu	IDMS	05/18/11	2.49E-03	2.62E-03	1.0	5.2
²⁴¹ Pu	IDMS	05/18/11	3.18E-04	3.38E-04	1.4	6.2
²⁴² Pu	IDMS	05/18/11	7.82E-04	8.22E-04	1.4	5.1
¹⁰³ Rh	ICPMS	10/21/10	4.70E-04	4.85E-04	5.0	3.2
¹⁰¹ Ru	ICPMS	10/21/10	8.25E-04	8.18E-04	5.0	-0.8
¹⁴⁷ Sm	IDMS	02/07/11	2.62E-04	2.60E-04	1.0	-0.8
¹⁴⁸ Sm	IDMS	02/07/11	1.91E-04	1.91E-04	1.0	0.0
¹⁴⁹ Sm	IDMS	02/07/11	2.44E-06	2.34E-06	2.7	-4.1
¹⁵⁰ Sm	IDMS	02/07/11	3.16E-04	3.17E-04	1.0	0.3
¹⁵¹ Sm	IDMS	02/07/11	7.74E-06	7.72E-06	2.5	-0.3
¹⁵² Sm	IDMS	02/07/11	1.10E-04	1.09E-04	1.0	-0.9
¹⁵⁴ Sm	IDMS	02/07/11	4.43E-05	4.40E-05	1.0	-0.7
⁹⁰ Sr	Beta counting	12/01/10	2.54E-04	2.30E-04	5.0	-9.4
²³⁴ U	IDMS	02/01/11	1.64E-04	1.65E-04	5.0	0.6
²³⁵ U	IDMS	02/01/11	3.85E-03	3.79E-03	1.4	-1.6
²³⁶ U	IDMS	02/01/11	3.64E-03	3.65E-03	1.4	0.3
²³⁸ U	IDMS	02/01/11	8.23E-01	8.23E-01	1.0	0.0

^a RSD, one sigma uncertainty

^b Relative difference between measurement in S1 and S2: $(S2/S1 - 1) \times 100$

^c All "ICPMS" in this table refers to "ICPMS with external calibration"

^d The alphas emitted by ²³⁸Pu and ²⁴¹Am were measured together due to their proximity in energies. The interference from ²⁴¹Am was separated out using the mass quantity of ²⁴¹Am measured using gamma spectrometry. The alpha measurements were calibrated using standard sources.

^e Quantities of all Pu isotopes were measured using IDMS, but the IDMS measurement of ²³⁸Pu was interfered by the residual ²³⁸U in the sample even after the U/Pu separation. Alpha spectrometry was also performed to measure the alphas from ²³⁸Pu and the combined alphas from ²³⁹Pu and ²⁴⁰Pu (due to their proximity). The alpha from ²³⁸Pu and the combined alphas from ²³⁹Pu and ²⁴⁰Pu, together with the measured quantities of ²³⁹Pu and ²⁴⁰Pu by IDMS, were used to derive the quantity of ²³⁸Pu in the sample.

6.2. Comparison to measurement of Sample P

As shown in Table 2, the burnup of sample P differs from that of samples S1 and S2 by only ~1.5%; therefore, it is expected that the isotope concentrations in all these three samples are not significantly different. Because sample P was measured at different laboratories (PNNL and KRI), it provides an independent cross check of the ORNL measurements. Since sample P was measured more than twenty years prior to the ORNL measurements, adjustments to some isotopes are needed to account for the additional cooling time to enable direct comparisons against samples S1 and S2 (measured around 2011). Correction factors were estimated using ORIGEN by simulating sample P and decaying the results to the measurement dates of samples S1 and S2. Table 7 shows the measured concentrations in sample P, the associated uncertainties, adjusted concentrations, and the comparison between the average of (S1, S2) and the adjusted concentration in sample P. For the majority of isotopes shown in Table 7, the relative differences between the average of (S1, S2) and P are small, but there are a few exceptions—as highlighted with gray background in the table—for which the relative difference is larger than 3 times RSD of the measurement uncertainty: ²⁴¹Am, ¹⁵¹Eu, ¹⁵²Eu, ¹⁵⁶Gd, ¹⁵⁷Gd, ²³⁸Pu, ¹⁴⁹Sm, ¹⁵⁴Sm, and ²³⁵U. Special attention was devoted to these isotopes in the subsequent analysis. As shown in Table 2, Samples S1 and S2 were taken from an axial location of the fuel rod that was ~100 cm higher than for sample P, where the moderator density is about 3.7% lower than that for sample P. The neutron spectra at samples S1 and S2 location are expected to be harder and lead to a higher plutonium production. This is the case, as reflected in the ratios for plutonium; for example, ²³⁹Pu measured in samples S1 and S2 was 2.7% higher than that measured in sample P, although the burnups in samples S1 and S2 were ~1.5% lower. Note the relatively large difference (8.6%) in ²³⁸Pu between the average of (S1, S2) and P, which cannot be explained by the small difference in burnup.

Table 7. Comparison of measured data in Samples P, S1, and S2

Isotope	Sample P		Samples S1, S2		Rel. diff. (%)
	Measured concentration (mg/g fuel) [5]	Measurement RSD (%)	Adjusted concentration ^a (mg/g fuel)	Avg. measured concentration (mg/g fuel)	Avg.(S1+S2)/P-1
²⁴¹ Am	3.82E-01	5.2	1.10E-03	8.86E-04	-19.5
¹³³ Cs	1.24E+00	--	1.24E-03	1.20E-03	-3.6
¹³⁵ Cs	4.30E-01	14.1	4.30E-04	4.18E-04	-2.8
¹³⁷ Cs	1.26E+00	3.8	7.22E-04	6.69E-04	-7.4
¹⁵¹ Eu	3.03E-03	3.4	6.40E-06	2.51E-06	-60.8
¹⁵² Eu	3.94E-04	3.4	1.73E-07	8.82E-08	-49.0
¹⁵³ Eu	1.42E-01	3.4	1.42E-04	1.32E-04	-7.0
¹⁵⁴ Eu	1.04E-02	7.0	2.83E-06	2.55E-06	-10.1
¹⁵⁵ Eu	1.60E-03	6.9	1.54E-07	1.55E-07	0.6
¹⁵⁴ Gd	1.76E-02	3.9	2.34E-05	2.89E-05	23.3

¹⁵⁵ Gd	8.78E-03	3.9	1.02E-05	1.02E-05	-0.5
¹⁵⁶ Gd	8.40E-02	3.9	8.40E-05	1.43E-04	69.6
¹⁵⁷ Gd	4.31E-03	3.9	4.31E-06	2.80E-07	-93.5
¹⁵⁸ Gd	1.82E-02	3.9	1.82E-05	2.23E-05	22.5
¹⁴³ Nd	7.63E-01	1.9	7.63E-04	7.82E-04	2.4
¹⁴⁴ Nd	1.64E+00	--	1.65E-03	1.63E-03	-1.5
¹⁴⁵ Nd	7.44E-01	1.9	7.44E-04	7.31E-04	-1.8
¹⁴⁶ Nd	8.30E-01	--	8.30E-04	8.21E-04	-1.1
¹⁴⁸ Nd	4.28E-01	--	4.28E-04	4.27E-04	-0.2
¹⁵⁰ Nd	2.08E-01	--	2.08E-04	2.07E-04	-0.7
²³⁷ Np	4.71E-01	2.5	4.98E-04	5.25E-04	5.3
²³⁸ Pu	2.69E-01	2.3	2.22E-04	2.03E-04	-8.6
²³⁹ Pu	4.36E+00	2.3	4.35E-03	4.47E-03	2.7
²⁴⁰ Pu	2.54E+00	2.3	2.58E-03	2.56E-03	-0.8
²⁴¹ Pu	1.02E+00	2.3	3.19E-04	3.28E-04	2.8
²⁴² Pu	8.40E-01	2.3	8.40E-04	8.02E-04	-4.5
¹⁴⁷ Sm	2.72E-01	3.8	2.77E-04	2.61E-04	-5.8
¹⁴⁸ Sm	1.98E-01	3.8	1.98E-04	1.91E-04	-3.5
¹⁴⁹ Sm	4.02E-03	7.6	4.02E-06	2.39E-06	-40.5
¹⁵⁰ Sm	3.21E-01	3.8	3.21E-04	3.17E-04	-1.4
¹⁵¹ Sm	9.45E-03	5.1	8.35E-06	7.73E-06	-7.4
¹⁵² Sm	1.17E-01	4.3	1.17E-04	1.10E-04	-6.4
¹⁵⁴ Sm	4.97E-02	3.8	4.97E-05	4.42E-05	-11.2
⁹⁰ Sr	4.78E-01	3.8	2.72E-04	2.42E-04	-11.0
²³⁴ U	1.20E-01	2.3	1.59E-04	1.65E-04	3.5
²³⁵ U	3.54E+00	2.3	3.54E-03	3.82E-03	7.9
²³⁶ U	3.69E+00	2.3	3.70E-03	3.65E-03	-1.5
²³⁸ U	8.25E+02	2.3	8.25E-01	8.23E-01	-0.2

^a adjusted for the extra decay time from the measurement date of sample P to those for samples S1 and S2 to enable direct comparison

6.3. Comparison of measured and calculated data

Fig. 8 illustrates the relative difference (%) between calculated (C) and measured (M) quantities of selected actinides in samples S1, S2, and P. Because samples S1 and S2 were extracted from adjacent fuel pellets from the same fuel rod and they have similar burnups, the combined (or average) values of these two samples are plotted in this figure for brevity. The mean value of the historical data, as observed in spent fuel samples analyzed in prior validation studies [15], are also plotted in this figure with error bars, which show one standard deviation of the C/M -1 values among the considered number of samples. The calculated results for samples S1 and S2 using SCALE 6.1.3 were also shown, in addition to the ones obtained with SCALE 6.2, for reference. As shown, the SCALE 6.2 results have better or similar agreements with measurements for most actinides in samples S1 and S2 than those obtained with SCALE 6.1.3 except for ²³⁸Pu. Significant speedup (~4×) for SCALE 6.2 has been observed in running these models when compared to SCALE 6.1.3.

The discussion related to samples S1, S2, and P in this section is based on SCALE 6.2 calculations. The historical data were based on SCALE 6.1 with ENDF/B-VII.0 library. As shown in Table 8, for all actinides except ²³⁶U and ²³⁸Pu, samples S1+S2 and sample P fall under the historical range. Slight over-estimations are observed for ²³⁶U. Historically, burnup codes (including several leading ones) tend to under-estimate ²³⁸Pu by 7–14% [15]. This problem has been largely resolved with the neutron cross sections in ENDF/B-VII.1 library (as used by SCALE 6.2), which is evident by the good agreement in ²³⁸Pu for sample P. However, there is still large discrepancy (14.37%) in ²³⁸Pu for samples S1 and S2, which is likely due to an underestimate in the measurement for this isotope rather than a calculation problem. As shown in Table 7, measured ²³⁸Pu is 8.6% less in samples S1 and S2 than that in sample P, although the burnup of samples S1 and S2 was only ~1.5% lower. Reviews of the ORNL measurement data did not determine a reason for the low bias. However, give the small quantities of ²³⁸Pu compared with other Pu isotopes (e.g., ²³⁹Pu and ²⁴⁰Pu), a minor mishandling in the measurement can lead to significant errors in ²³⁸Pu. Further investigation is recommended on this issue in future work.

Comparisons can also be made between the previous PNNL and KRI measurement (on sample P) and the recent ORNL measurement (on samples S1 and S2). First of all, the ORNL measurement was performed ~20 years after the PNNL and KRI measurement on samples from the same fuel rod, which makes the ORNL measurement more challenging because for many isotopes (e.g., ²⁴¹Pu) there are smaller quantities left in the fuel due to the additional decay time. However, for all actinides except for ²³⁸Pu, the ORNL measurement agreed well with the PNNL and KRI measurement. Note that ²⁴³Am and ²⁴⁴Cm were not

measured for Sample P. ^{244}Cm is normally difficult to measure, but the ORNL measurement performed exceedingly well compared to calculation. Table 8 lists the measured and calculated actinide isotope concentrations in the three samples. This table also includes comparisons between calculation and measurement, and the historical data for reference, as shown in Fig. 8. The calculation results for samples S1, S2, and P were based on SCALE 6.2 and ENDF/B-VII.1 nuclear data libraries, whereas the calculation results for historical data were based on SCALE 6.1 and ENDF/B-VII.0 nuclear data libraries. The mean value of the historical data refers to the average $C/M - 1$ value among prior spent fuel samples as concluded in a previous study [15], whereas σ is the standard deviation of the distribution of those $C/M - 1$ values.

Fig. 8. Relative difference (%) of actinides between calculation (C) and measurement (M) for samples S1, S2, and P. (Samples S1 and S2 were measured at ORNL around 2011, whereas sample P was measured at PNNL in 1987 and at KRI in 1995.)

Table 8. Measured and calculated isotope content in sample P and the combined samples of S1 and S2.

Sample	Measured (M) quantity		Measurement		Calculated (C) quantity		C/M - 1		Historical data	
	g/g_fuel		uncertainty (%)		g/g_fuel		%		data	
	P	avg (S1, S2)	P	S1, S2	P	avg (S1, S2)	P	avg (S1, S2)	Mean*	σ^{**}
²⁴¹ Am	3.82E-04	8.85E-04	5.2	5.0	3.42E-04	1.03E-03	-10.29	15.89	10.2	20.7
²⁴³ Am	--	1.72E-04	--	5.0	--	1.79E-04	--	4.30	2.9	14
²⁴⁴ Cm	--	2.94E-05	--	5.0	--	2.93E-05	--	-0.41	-4.4	11.1
²³⁷ Np	4.71E-04	5.24E-04	2.5	5.0	4.74E-04	5.08E-04	0.68	-3.16	3.9	19.5
²³⁸ Pu	2.69E-04	2.03E-04	2.3	5.0	2.73E-04	2.32E-04	1.51	14.37	-11.7	5.9
²³⁹ Pu	4.36E-03	4.47E-03	2.3	1.0	4.51E-03	4.62E-03	3.46	3.34	4.1	3.5
²⁴⁰ Pu	2.54E-03	2.56E-03	2.3	1.0	2.57E-03	2.64E-03	1.24	3.17	2.2	3.4
²⁴¹ Pu	1.02E-03	3.28E-04	2.3	1.4	1.01E-03	3.24E-04	-1.19	-1.40	-1.4	4.5
²⁴² Pu	8.40E-04	8.02E-04	2.3	1.4	8.05E-04	8.02E-04	-4.15	-0.09	-5.9	6.1
²³⁴ U	1.20E-04	1.64E-04	2.3	5.0	1.26E-04	1.73E-04	4.75	5.36	12.4	17.6
²³⁵ U	3.54E-03	3.82E-03	2.3	1.4	3.62E-03	3.79E-03	2.29	-0.84	1.2	3.5
²³⁶ U	3.69E-03	3.64E-03	2.3	1.4	3.76E-03	3.77E-03	2.01	3.35	-1.9	3.5
²³⁸ U	8.25E-01	8.23E-01	2.3	1.0	8.24E-01	8.24E-01	-0.13	0.10	-0.1	0.4

*: the mean deviation between measurement and calculation (C/M-1) found in prior spent fuel samples [15].

**: the standard deviation of the distribution of the C/M -1 values in the prior spent fuel samples [15].

Fig. 9 shows the comparison for selected fission products measured in samples S1, S2, and P, and Table 9 lists the measured and calculated fission product contents in all samples and the comparisons between them. Note that ¹⁴⁹Sm, ¹⁵⁴Gd, ¹⁵⁶Gd, and ¹⁵⁸Gd were included in the table but not in the figure because of the large C/M discrepancies (>35%) in sample P that would make the figure less readable, especially for the isotopes with small discrepancies. Similarly, the historical data range is also included in both the figure and the table for reference. As shown, the SCALE 6.2 results for samples S1 and S2 have better or similar agreements to measurement for most fission products shown in this plot than those obtained with SCALE 6.1.3. For the SCALE 6.1 and 6.2 results of samples S1 and S2, all fission products except for ⁹⁰Sr and ¹⁵¹Sm are consistent with the historical range of similar calculated results. ⁹⁰Sr was measured using beta counting, which has larger uncertainty than the IDMS method. ¹⁵¹Sm is a low abundance isotope. This explains the larger discrepancies in samples S1 and S2 for this isotope. As noted in Table 9, there are 8 fission products that were not measured in sample P (the PNNL and KRI measurements): ¹⁴⁰Ce, ¹⁴²Ce, ¹⁶⁰Gd, ¹³⁹La, ⁹⁵Mo, ¹⁴²Nd, ¹⁰³Rh, and ¹⁰¹Ru. The ORNL measurement has better agreement with calculation than the PNNL and KRI measurement for 4 fission products: ¹⁵⁴Gd, ¹⁵⁶Gd, ¹⁵⁸Gd, and ¹⁴⁹Sm, but worse for ¹³³Cs, ¹³⁵Cs, and ¹³⁷Cs and much worse for ¹⁵⁴Eu and ⁹⁰Sr. The relative differences between calculation and measurement for ¹³⁷Cs and ¹⁵⁴Eu in samples S1 and S2 are 4.73% and 17.36%, respectively. For the remaining fission products, the ORNL measurement compared well with the PNNL and KRI measurement.

The differences in the ¹³⁷Cs and ¹⁵⁴Eu results, and bias observed in several other fission products, could suggest overestimation of the burnup based on measured ¹⁴⁸Nd. However, review of the ¹³⁷Cs gamma scan made at PNNL (Fig. 5) indicates that the expected relative difference in the burnup between sample P and samples S1 and S2 is about 2%, which is somewhat consistent with the burnup estimated using ¹⁴⁸Nd (Table 2). Also, comparison of the PNNL and ORNL measurements for ¹³⁷Cs, and ¹⁵⁴Eu indicate that the discrepancies are likely attributed to bias in the ORNL measurements for these nuclides, and not due to the ¹⁴⁸Nd burnup estimate. Caesium is volatile and is known to migrate from fuel matrix to free surfaces (e.g., the gap between fuel and cladding) when the fuel is irradiated under high temperatures, which might have caused less-than-expected quantities of caesium isotopes measured in these ORNL samples.

Fig. 9. Relative difference (%) of selected fission products between calculation (C) and measurement (M) for samples S1, S2, and P.

Table 9. Measured and calculated isotope content in sample P and the combined samples of S1 and S2.

Sample	Measured (M) quantity		Measurement		Calculated (C) quantity		C/M - 1		Historical data	
	g/g _{fuel}		uncertainty (%)		g/g _{fuel}		%		%	
	P	avg(S1, S2)	P	S1, S2	P	avg(S1, S2)	P	avg(S1, S2)	Mean*	σ^{**}
¹⁴⁰ Ce	--	1.35E-03	--	1.0	--	1.39E-03	--	2.90	--	--
¹⁴² Ce	--	1.22E-03	--	1.0	--	1.27E-03	--	3.92	--	--
¹³³ Cs	1.24E-03	1.20E-03	--	1.0	1.25E-03	1.25E-03	1.14	4.39	1.9	1.7
¹³⁵ Cs	4.30E-04	4.18E-04	14.1	1.0	4.44E-04	4.53E-04	3.30	8.32	2.7	3.7
¹³⁷ Cs	1.26E-03	6.69E-04	3.8	1.0	1.22E-03	7.00E-04	-2.79	4.73	-0.7	3.1
¹⁵³ Eu	1.42E-04	1.32E-04	3.4	1.0	1.35E-04	1.35E-04	-4.79	2.70	-0.9	3.1
¹⁵⁴ Eu	1.04E-05	2.54E-06	7.0	2.1	1.07E-05	2.98E-06	3.43	17.36	4.2	10.4
¹⁵⁵ Eu	1.60E-06	1.55E-07	6.9	15.0	1.64E-06	1.58E-07	2.65	1.32	-4.4	7.7
¹⁵⁴ Gd	1.76E-05	2.89E-05	3.9	1.0	2.40E-05	3.23E-05	35.92	12.06	--	--
¹⁵⁵ Gd	8.78E-06	1.01E-05	3.9	1.0	8.99E-06	1.05E-05	2.42	3.75	-8.4	14.4
¹⁵⁶ Gd	8.40E-05	1.42E-04	3.9	1.0	1.44E-04	1.43E-04	70.88	0.33	--	--
¹⁵⁸ Gd	1.82E-05	2.23E-05	3.9	1.0	2.55E-05	2.56E-05	40.14	14.73	--	--
¹⁶⁰ Gd	--	1.66E-06	--	2.7	--	1.51E-06	--	-9.37	--	--
¹³⁹ La	--	1.49E-03	--	5.0	--	1.38E-03	--	-7.15	--	--
⁹⁵ Mo	--	8.25E-04	--	5.0	--	8.30E-04	--	0.58	--	--
¹⁴² Nd	--	3.19E-05	--	1.4	--	3.19E-05	--	0.19	--	--
¹⁴³ Nd	7.63E-04	7.81E-04	1.9	1.0	7.73E-04	7.81E-04	1.25	-0.06	0.8	3.2
¹⁴⁴ Nd	1.64E-03	1.62E-03	--	1.0	1.60E-03	1.58E-03	-2.69	-2.40	--	--
¹⁴⁵ Nd	7.44E-04	7.31E-04	1.9	1.0	7.33E-04	7.31E-04	-1.43	0.05	-0.5	2.2
¹⁴⁶ Nd	8.30E-04	8.21E-04	--	1.0	8.21E-04	8.18E-04	-1.12	-0.34	--	--
¹⁴⁸ Nd	4.28E-04	4.27E-04	--	1.0	4.28E-04	4.27E-04	-0.01	0.01	0.6	1.4
¹⁵⁰ Nd	2.08E-04	2.06E-04	--	1.0	2.13E-04	2.13E-04	2.51	3.29	--	--
¹⁰³ Rh	--	4.77E-04	--	5.0	--	5.32E-04	--	11.52	9.1	10.9
¹⁰¹ Ru	--	8.22E-04	--	5.0	--	8.96E-04	--	9.04	5.8	12.3
¹⁴⁷ Sm	2.72E-04	2.61E-04	3.8	1.0	2.59E-04	2.64E-04	-4.54	1.15	1.6	3.4
¹⁴⁸ Sm	1.98E-04	1.91E-04	3.8	1.0	1.85E-04	1.86E-04	-6.71	-2.80	--	--
¹⁴⁹ Sm	4.02E-06	2.39E-06	7.6	2.7	2.16E-06	2.25E-06	-46.21	-6.06	1.9	6.2
¹⁵⁰ Sm	3.21E-04	3.16E-04	3.8	1.0	3.27E-04	3.27E-04	1.96	3.24	0.8	3.2
¹⁵¹ Sm	9.45E-06	7.73E-06	5.1	2.7	8.90E-06	8.19E-06	-5.84	5.92	-2.1	4.4
¹⁵² Sm	1.17E-04	1.10E-04	4.3	1.0	1.14E-04	1.12E-04	-2.63	1.98	1.6	3.7
¹⁵⁴ Sm	4.97E-05	4.42E-05	3.8	1.0	4.69E-05	4.69E-05	-5.66	6.19	--	--
⁹⁰ Sr	4.78E-04	2.42E-04	3.8	5.0	4.87E-04	2.76E-04	1.94	14.12	-0.9	6.9

*: the mean deviation between measurement and calculation (C/M-1) found in prior spent fuel samples [15].

**: the standard deviation of the distribution of the C/M -1 values in the prior spent fuel samples [15].

6.4. Summary of outlier isotopes

Table 10 and Table 11 list the isotopes, determined to be outliers based on the various comparisons made in this work, in samples S1 and S2, and in Sample P, respectively. To facilitate comparisons, both tables also list the measured and calculated quantities, the measured relative isotope mass (percent of a particular isotope mass versus overall elemental mass measured), and the deviations between measurement and calculation in each of the three samples. Except for ²³⁸Pu, all isotopes listed in Table 10 have less than 1% relative isotope mass, which implies large uncertainties are likely associated with the measurement of these low concentration isotopes. For ²³³U the sample dilutions measured by ICPMS for the uranium isotopes resulted in small measured mass counts above background that resulted in large relative standard deviations of ~40%. Therefore, the observed

large discrepancy between measurement for ^{233}U was likely due to the large uncertainties in the measurement of this isotope. As discussed in the previous subsection, ^{238}Pu was likely underestimated in the measurement of samples S1 and S2. As shown in Table 11, for ^{151}Eu , ^{154}Gd , ^{156}Gd , ^{158}Gd , and ^{149}Sm , there are large discrepancies between measurement and calculation in Sample P, whereas the discrepancies are much smaller in Samples S1 and S2. Because the calculations for all these three samples were performed in a consistent way, it is likely that issues were present in the P measurements for these isotopes. For ^{149}Sm , the mean discrepancy was -6% in the average of samples S1 and S2, whereas it was -46.2% in sample P, which suggests the measurement of this isotope in Sample P was likely problematic. For the remaining two isotopes, ^{152}Eu and ^{157}Gd , there are large discrepancies between measurement and calculation in all three samples. The relative isotope masses of these two isotopes are less than 4%, which implies that the measurement uncertainties for these two isotopes are likely to be large, which is evident by the poor agreements among the measured values in all the three samples (shown in Table 6 and Table 7).

Table 10. Outlier isotopes in samples S1 and S2

Isotope	Samples S1, S2			Sample P	
	g/g fuel, M	%relative isotope mass, M	g/g fuel, C	C/M-1, %	C/M-1, %
^{152}Eu	8.80E-08	0.060	2.32E-09	-97.4	-98.7
^{152}Gd	7.93E-08	0.040	3.62E-08	-54.4	--
^{157}Gd	2.80E-07	0.140	1.02E-07	-63.6	-97.8
^{238}Pu	2.03E-04	2.160	2.32E-04	14.37	1.5
^{233}U	4.76E-05	0.006	6.66E-09	-100.0	--

Table 11. Outlier isotopes in sample P

Isotope	Sample P			Samples S1, S2	
	g/g fuel, M	%relative isotope mass, M	g/g fuel, C	C/M-1, %	C/M-1, %
^{151}Eu	3.03E-06	1.92	9.31E-07	-69.3	17.6
^{152}Eu	3.94E-07	0.25	4.93E-09	-98.7	-97.4
^{154}Gd	1.76E-05	13.27	2.40E-05	36.4	12.1
^{156}Gd	8.40E-05	63.19	1.44E-04	71.4	0.3
^{157}Gd	4.31E-06	3.24	9.53E-08	-97.8	-63.6
^{158}Gd	1.82E-05	13.70	2.55E-05	40.1	14.7
^{149}Sm	4.02E-06	0.41	2.16E-06	-46.2	-6.0

7. Conclusions

The design, safety and licensing of spent nuclear fuel facilities relies on accurate computational methods underpinned by high quality experimental data. These new Calvert Cliffs spent fuel measurements performed at ORNL provide valuable data to the nuclear community with additional measurements for isotopes important to various spent fuel applications. Before these data are used in safety applications, it is important to assess their quality. This work has demonstrated and quantified the accuracy of these isotope measurements by performing (1) consistency check between the measurements of the two ORNL samples, (2) comparison to the measurement on similar sample conducted at PNNL and KRI, (3) comparison to historical data, (4) comparison to calculated results generated using detailed burnup simulation models. These comparisons demonstrated that ORNL has similar capabilities to perform DA measurements on spent fuel as other leading institutes. The results for most isotopes, except for ^{236}U , ^{238}Pu , ^{154}Eu , ^{151}Sm , and ^{90}Sr , in the three samples studied in this work are within the range as defined by historical data. Although the ORNL measurement was more challenging than the PNNL and KRI measurement for some of the isotopes due to 20 years of extra decay time, the ORNL measurements were found to be comparable to the PNNL and KRI measurements in general. For most actinides, including ^{235}U , ^{239}Pu , and ^{242}Pu , the ORNL measurements had better or comparably good agreements to corresponding calculated values than the PNNL measurements. The quantities of ^{244}Cm in the ORNL measurement agreed with calculation exceedingly well. However, ^{238}Pu seemed to be significantly underestimated in the ORNL measurements, for which the root cause needs to be further investigated. For several fission products (^{133}Cs , ^{135}Cs , ^{137}Cs , ^{154}Eu , and ^{90}Sr), the ORNL measurements did not compare as well with calculation as the PNNL-KRI measurements did. However, for the other 18 fission products, the ORNL measurement provided better or comparable agreement with the calculation than the PNNL-KRI measurements. In summary, and as shown in this study, the new ORNL measurements provide high quality DA data

for 22 isotopes in spent fuel with relatively high burnup and long cooling time, and they can serve as good benchmark data for nuclear burnup code validation and many other spent fuel studies. This study also shows that SCALE 6.2 results had better or comparable agreements to measurement on most of the considered isotopes than the SCALE 6.1.3 results.

8. Acknowledgment

The spent fuel sample measurements at ORNL in 2011 were supported by the DOE's Office of Nuclear Energy and the National Nuclear Security Administration (NNSA). The computational modeling and analysis of the measurement data were supported by the Next Generation Safeguards Initiative program (NGSI), the Office of Nonproliferation and Arms Control of NNSA. The authors thank John Scaglione of ORNL for documentation on the gamma scan and cutting of the ORNL samples from the Calvert Cliffs fuel rod segment. The authors would like to thank all those who have reviewed this manuscript.

References

- [1] I. C. Gauld, J. M. Giaquinto, J. S. Delashmitt, J. Hu, T. J. Haverlock and C. Romano, "Re-evaluation of spent nuclear fuel assay data for the Three Mile Island unit 1 reactor and application to code validation," *Annals of Nuclear Energy*, vol. 87, pp. 267-281, 2016.
- [2] B. T. Rearden and M. A. Jessee, "SCALE Code System, Version 6.2," ORNL/TM-2005/39, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 2016.
- [3] R. J. Guenther, D. E. Blahnik, U. P. Jenquin, J. E. Mendel, L. E. Thomas and C. K. Thornhill, "Characterization of Spent Fuel Approved Testing Material—ATM-104," Pacific Northwest Laboratory, PNL-5109-104 (UC-802), 1991.
- [4] G. Radulescu, I. Gauld and G. Ilas, "SCALE 5.1 Predictions of PWR Spent Nuclear Fuel Isotopic Compositions," Oak Ridge National Laboratory, ORNL/TM-2010/44, 2010.
- [5] G. Ilas, I. C. Gauld, F. C. Difilippo and M. B. Emmett, "Analysis of Experimental Data for High Burnup PWR Spent Fuel Isotopic Validation - Calvert Cliffs, Takahama, and Three Mile Island Reactors," U. S. Nuclear Regulatory Commission, NUREG/CR-6968 (ORNL/TM-2008/071), 2008.
- [6] J. Hu, I. C. Gauld, J. Banfield and S. Skutnik, "Developing Spent Fuel Assembly Standards for Advanced NDA Instrument Calibration – NGSI Spent Fuel Project," Oak Ridge National Laboratory report, ORNL/TM-2013/576, 2014.
- [7] J. M. Scaglione, *Scientific Notebook of Calvert Cliffs Unit 1 Spent Fuel Samples*, Oak Ridge National Laboratory, SN-SNL-SCI-052, 2009.
- [8] J. M. Scaglione, "Three Mile Island Unit 1 Radiochemical Assay Comparisons to SAS2H Calculations," Yucca Mountain Project Report, CAL-UDC-NU-000011, Rev. A, 2002.
- [9] Bechtel SAIC Company, "Summary Report of Commercial Reactor Criticality Data for Three Mile Island Unit 1," TDR-UDC-NU-000004 Rev 01, Las Vegas, Nevada, 2001.
- [10] J. S. Delashmitt, R. D. Canaan, J. M. Giaquinto, R. R. Smith and B. K. Woody, "High Precision Hot Cell Dissolution Protocol for Irradiated Mixed Oxide Fuels," in *Institute of Nuclear Materials*

Management 52nd Annual Meeting, 2011.

- [11] ASTM, Standard Test Method for Atom Percent Fission in Uranium and Plutonium Fuel (Neodymium-148 Method), Annual Book of ASTM Standards, 12.02(E321–79), p. 91, 1995.
- [12] "GUM Workbench Professional Version 2.4," [Online]. Available: http://www.metrodata.de/ver24_en.html.
- [13] D. Boulanger, M. Lippens, L. Mertens and e. al., "High burnup PWR and BWR MOX fuel performance: A review of BERGONUCLEAIRE recent experimental programs," in *2004 Int. LWR Fuel Performance Mtg*, Orlando, Florida, 2004.
- [14] I. C. Gauld, G. Radulescu, G. Ilas, B. D. Murphy, M. L. Williams and D. Wiarda, "Isotopic Depletion and Decay Methods and Analysis Capabilities in SCALE," *Nucl. Technol.*, vol. 174, no. 2, pp. 169-195, 2011.
- [15] G. Ilas, I. C. Gauld and G. Radulescu, "Validation of new depletion capabilities and ENDF/B-VII data libraries in SCALE," *Annals of Nuclear Energy*, vol. 46, pp. 43-55, 2012.
- [16] M. DeHart and S. Bowman, "Reactor Physics Methods and Analysis Capabilities in SCALE," *Nuclear Technology*, vol. 174, no. 2, pp. 196-213, May 2011.
- [17] The SCALE team, "SCALE: A Comprehensive Modeling and Simulation Suite for Nuclear Safety Analysis and Design," ORNL/TM-2005/39, Version 6.1, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 2011.