

Analysis of isotopic assay data from the MALIBU program

Germina Ilas*, Ian C. Gauld

Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA

Abstract

Acquisition and analysis of experimental isotopic assay data are essential for validating computer code predictions of isotopic composition for spent nuclear fuel in order to establish the uncertainty and bias associated with code predictions. Recently available experimental data for uranium oxide spent fuel, acquired through the MALIBU international program, are analyzed in this paper. The analyzed measurements include extensive actinide and fission product data of importance to spent fuel safety applications, including burnup credit, decay heat, and radiation source terms. Analysis of the measurements was performed using the two-dimensional depletion module TRITON in the SCALE computer code system.

1. Introduction

Nuclear fuel being discharged from commercial reactors is achieving progressively higher burnup through the use of higher initial enrichments, improved assembly designs, and more efficient fuel management strategies. At this time, most of the publicly available data correspond to relatively low burnup fuel, and any assessment of the uncertainty in the predicted inventory for high burnup fuel involves extrapolation well beyond the range of experimental data available for code validation. A reassessment of the uncertainties in computer model predictions in the domains of increased enrichment, burnup, and cooling time is essential to understanding the associated uncertainties in the code predictions for spent fuel transportation and storage applications including decay heat, radiation sources, and criticality safety evaluations that use burnup credit. Acquisition and analysis of additional

experimental data are required for this goal to be achieved.

Recently available radiochemical isotopic assay data, measured through the first phase of the MALIBU international program (Boulanger et al., 2004; Malibu Program, 2004), are analyzed in this paper for application to code validation. The MALIBU program, coordinated by Belgonucleaire, is designed to provide a large set of reliable experimental isotopic data with low uncertainties for high burnup commercial spent nuclear fuel. The program includes participants from laboratories and utilities from seven countries: Belgium, France, Germany, Japan, Switzerland, Sweden, and the United States. Oak Ridge National Laboratory (ORNL) has participated in the program through support of the U.S. Department of Energy and the U.S. Nuclear Regulatory Commission.

A key feature of the first phase of the program was that three cross-checking laboratories

* Corresponding author, ilasg@ornl.gov.
Tel: +01 (865) 241 4672; Fax: +01 (865) 574 9619.

participated in radiochemical assay measurements to reduce the experimental uncertainties and improve confidence in the measured data: Studiecentrum voor Kernenergie - Centre d'Étude de l'Énergie Nucléaire (SCK-CEN) in Belgium, Commissariat à l'Énergie Atomique (CEA) in France, and Paul Scherrer Institute (PSI) in Switzerland. The spent fuel measurements include extensive actinide and fission product data of importance to spent fuel safety applications. Measurements have been carried out on both uranium oxide (UO₂) and mixed oxide (MOX) fuels between 2004 and 2006. Only the UO₂ fuel measurement data are discussed in this paper.

2. Background on UO₂ fuel measurements

The UO₂ samples were selected from the same fuel rod of an assembly with an initial enrichment of 4.3 wt % ²³⁵U. This assembly was irradiated for four consecutive cycles in the Gösgen pressurized water reactor operated in Switzerland. The samples were selected from two fuel segments: one cut from the peak burnup region of the fuel rod and the other from the bottom part of the same fuel rod. The two fuel segments had an estimated burnup of 47 and 68 GWd/MTU. Two samples, each about the length of three fuel pellets, were selected from each segment to be measured at different laboratories. The samples will be identified in this paper as L1 and L2 (lower burnup) and H1 and H2 (higher burnup), and the three laboratories where these sample were measured as A, B, and C (no direct correspondence to the laboratories named previously). Samples L1 and L2 were analyzed at laboratories B and C. Samples H1 and H2 were measured by laboratories A and B.

Isotopic measurements of about 50 isotopes were performed for each sample, including isotopes of uranium, plutonium, neptunium, americium, curium, and many fission products important to source terms in spent fuel, burnup credit, and nuclear criticality safety applications. The nuclide concentrations in the measured samples were reported at the date of measurement and also at a reference date that was set close to the actual date of the measurements to minimize uncertainties associated with data adjustments. For metallic fission products (isotopes of antimony, rhodium, ruthenium, molybdenum, silver, strontium, and technetium) the results were reported for

measurements on both main solution and residue solution.

3. Assembly design and operation history data

The information on the fuel assembly geometry, irradiation history, and sample burnup that are necessary for developing a computational model to calculate the isotopic composition of the samples under consideration was provided through the MALIBU program. For the cases in which insufficient information was available, assumptions were made.

The fuel assembly that hosted the fuel rod from which samples were selected had a 15 × 15 configuration, with 205 fuel rods and 20 guide tubes. Data was available on the assembly geometry, irradiation cycle start and end dates, actual cycle duration, effective power days and down days, core load factor, concentration of soluble boron in moderator, operator-estimated sample burnup, and sample fuel temperature at the center and surface of the fuel rod.

The effective fuel temperature, T_{eff} , important parameter for resonance self-shielding calculations, was calculated (de Kruijff and Janssen, 1996) as shown in Eq. 1, based on the provided temperatures at the center (T_c) and surface (T_s) of the fuel pin, respectively.

$$T_{\text{eff}} = T_s + (4/9) (T_c - T_s) \quad (1)$$

The temperature $T(z)$ of the moderator at the sample axial location z with respect to the bottom of the active fuel region was calculated (Hermann et al., 1996) as

$$T(z) = T_{\text{in}} + [1 - \cos(\pi z/L)] [(T_{\text{out}} - T_{\text{in}})/2] \quad (2)$$

T_{in} and T_{out} in Eq. 2 represent the inlet and outlet temperatures of the coolant, and L is the active fuel rod length. Two moderator temperature values were calculated for the axial heights along the fuel rod that correspond to the center of the two fuel segments from which the samples were selected. Based on these temperature values, the corresponding moderator densities were determined by using tabulated temperature vs. pressure data (Haar and Kell, 1984) to correspond to the actual operating system pressure.

4. Computational analysis

4.1. Computational methods

The computational analysis of the measurements was carried out using the two-dimensional (2-D) depletion sequence TRITON in the SCALE computer code system (SCALE 5.1, 2006) that is developed and maintained at ORNL. TRITON couples the 2-D arbitrary polygonal mesh, discrete ordinates transport code NEWT with the depletion and decay code ORIGEN-S to perform the burnup simulation. At each depletion step, the transport flux solution from NEWT is used to generate cross sections for the ORIGEN-S calculation. The isotopic composition data resulting from ORIGEN-S are employed in the subsequent transport calculation to obtain cross sections for the next depletion step in an iterative manner throughout the irradiation history.

TRITON has the capability of individually simulating the depletion of multiple mixtures in a fuel assembly model. This is a very useful and powerful feature for a nuclide inventory analysis, as it allows a more appropriate representation of the local flux distribution and neutronic environment of the measured fuel rod in the assembly. The flux normalization in a TRITON calculation can be performed using either the power in a specified mixture, the total power corresponding to multiple mixtures, or the assembly power. The first option permits the burnup (power) in the measured sample to be input, usually inferred from measurement data of burnup indicators (such as ^{148}Nd).

All TRITON calculations for this paper employed the SCALE 44-group cross section library based on ENDF/B-V data and the NITAWL module in SCALE as the cross section processor. Default values were used for the convergence parameters in the NEWT transport calculation. All the 316 isotopes for which cross sections data are available in the multigroup transport library used with NEWT were applied in updating cross sections for the ORIGEN-S fuel depletion calculation at each depletion step.

4.2. Computational model

Individual TRITON models were developed for each of the measured samples. Taking advantage of the fuel assembly symmetry, a quarter assembly

model, as illustrated in Fig. 1, was used for the analysis. Reflective boundary conditions were imposed on all four boundaries of the configuration. All the details on geometry, material, and irradiation history data, as available, were included in the TRITON model. As indicated by the use of different colors in Fig. 1, individual depleting mixtures were specified for the measured rod and its nearest neighbor fuel rods; all other fuel rods were treated as a single depletion material with uniform composition, given that their impact on the neutron flux spectrum in the measured fuel rod is a second-order effect.

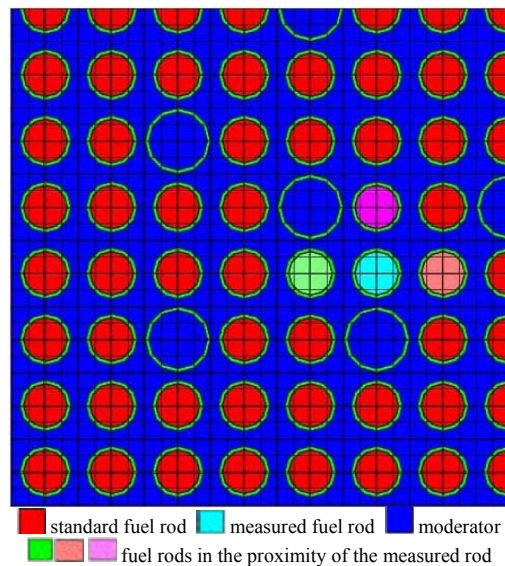


Fig. 1. TRITON depletion model (1/4 assembly).

In addition to the models used for the effective fuel temperature and moderator temperature as described previously, assumptions were used with respect to the sample power and burnup values used in the depletion simulations. In the calculation of the sample power, each reactor cycle was split in four depletion steps for the convenience of specifying the variation of the boron content in the coolant and to account for the core load factor data that were available for four time intervals during an irradiation cycle. It was assumed that the sample power variation during a cycle is similar to the core power variation as given by the load factor. For the coast-down depletion step in each of the irradiation cycles, a linear variation with time was assumed for the power, which was calculated as shown in Eq. 3,

where B stands for sample burnup, t for depletion time, subscript i for the depletion step number, and f_i for percentage load factor in step i.

$$P = [(f_{i-1} + f_i)/2] [(B_i - B_{i-1})/(t_i - t_{i-1})] \quad (3)$$

As the burnup estimated by the utility based on calculations performed by the utility is in general not sufficiently accurate for benchmark purposes, the burnup based on the measured values of burnup indicators is a widely used approach. The isotopes generally used as burnup indicators are fission products that are reliable indicators of the integral number of fissions occurring in the fuel during irradiation (Goodall and Johnson, 1997). High-precision measurements of these nuclides are desired in order to obtain reliable measures for the sample burnup.

In the MALIBU experimental program, the sample burnup was based on the measured values of the widely used burnup indicators ^{148}Nd and ^{137}Cs , as well as combinations of other neodymium isotopes. In the case of samples H1 and H2 measured by laboratories A and B, the burnup values determined from the measured ^{148}Nd differed by an amount significantly larger than the estimated experimental uncertainty for this nuclide. It was also observed from other two-way and three-way laboratory cross-check comparisons for several other measured samples (including MOX fuel) that the laboratory A showed higher measurement values for neodymium as compared to laboratories B and C, indicating a possible systematic bias in the neodymium results measured by laboratory A. Based on the cross check, the MALIBU program recommended that the measured ^{148}Nd should not be relied upon exclusively for burnup determination, and other potential burnup indicators should be used for this purpose. For the samples measured at laboratory A in particular, the consensus burnup value was based on the ^{137}Cs indicator only.

As samples H1 and H2 were selected from a fuel segment cut from the central region of the fuel rod that is characterized by a flat burnup profile, they are expected to have practically the same burnup and can be considered duplicate or “sister” samples for a unique sample, H. The burnup used for this high-burnup H sample depletion simulations in this paper was the average (70.3 GWd/MTU) of the two burnup values for samples H1 and H2 that were calculated based on measured data for burnup indicators. The burnup for sample H1 measured at laboratory A was calculated as 70.5 GWd/MTU

based on the measured ^{137}Cs . The burnup for sample H2 measured at laboratory B was determined as a weighted average (B_{avg}) of the two burnup values based on measured ^{137}Cs and ^{148}Nd . The measurement uncertainty was used as a weighting function in this latter case, as shown in Eq. 4, where B_i is the burnup calculated based on the measured burnup-indicating isotope i and σ_i is the measurement uncertainty for that isotope. The burnup resulted for sample H2 was 70.2 GWd/MTU. This value is within the experimental uncertainty of the burnup value determined based on measured data of ^{137}Cs for sample H1.

$$B_{\text{avg}} = (B_1/\sigma_1^2 + B_2/\sigma_2^2) / (1/\sigma_1^2 + 1/\sigma_2^2) \quad (4)$$

In the case of sample L1 measured at laboratory A, the burnup was estimated in this paper based on the measured concentration of ^{137}Cs . For sample L2 measured at laboratory C, the burnup was determined based on both ^{137}Cs and ^{148}Nd burnup indicators measured data, using Eq. 4. The resulting burnup values are 50.8 GWd/MTU for L1 and 46.0 GWd/MTU for L2, which differ by about 10%. Note that based on the gamma scan data for the fuel rod segment from which samples L1 and L2 were cut, the burnup difference is expected to be about 5–10%. As they were obtained from a region of the fuel rod characterized by a steep gradient of burnup as a function of axial location along the rod length, L1 and L2 represent two distinctive fuel samples rather than specimens of the same sample.

5. Results and discussion

The results of the comparison of the predicted and measured data, as percentage difference, are illustrated in Figs. 2–6 for samples identified as H, L1, and L2. The plotted data shows, for each nuclide, the value of (C/E-1) in percentage, where C/E represents the calculated-to-experimental concentration ratio. The measured isotopic concentration data recommended by the MALIBU program for sample H were determined as a weighted combination of the two sets of data reported for the “sister” samples H1 and H2 using a weighing similar to that expressed by Eq. 4.

The majority of the measured uranium and plutonium nuclides are predicted within 7% of the measurement for all samples, as illustrated in Fig. 2.

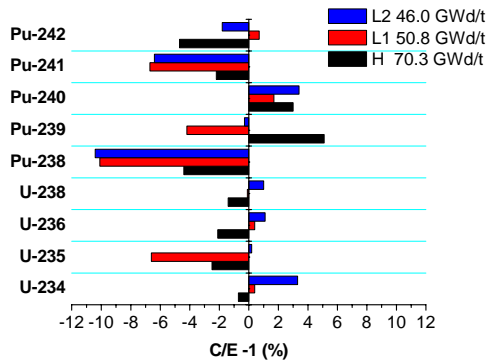


Fig. 2. Comparison calculation-experiment for major actinides.

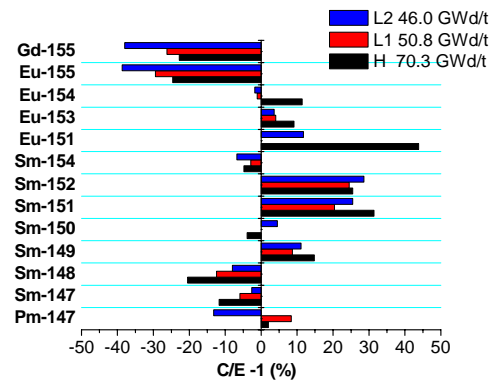


Fig. 5. Comparison calculation-experiment for Sm, Eu, Gd, and Pm isotopes.

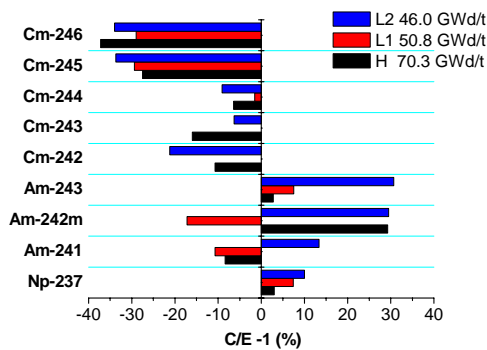


Fig. 3. Comparison calculation-experiment for minor actinides.

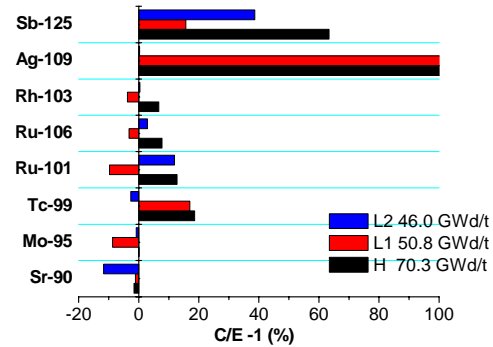


Fig. 6. Comparison calculation-experiment for metallic fission products.

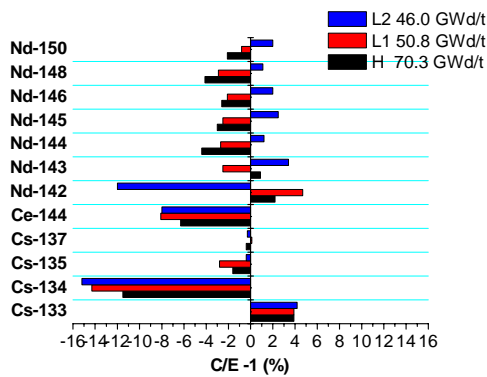


Fig. 4. Comparison calculation-experiment for Cs, Ce, and Nd isotopes.

The exception is ^{238}Pu , which is underestimated by about 10% in the samples L1 and L2. The predicted ^{235}U and ^{239}Pu concentration values in the high burnup sample H are similar to the reported experimental uncertainties.

The results of the comparison for the measured minor actinides are illustrated in Fig. 3. The ^{241}Am nuclide, a major contributor to decay heat, is estimated within 13% of the measurement. The results for all americium nuclides in sample L2 are consistently higher than those of the other two samples. This may be indicative of a systematic bias in the measurements for americium isotopes at laboratory C. This is supported by the observation that the bias observed in the results of laboratories A and B appear to be consistent with the bias in ^{241}Pu . At the time of the measurements, more than 85% of the ^{241}Am is produced by ^{241}Pu decay, and similar code bias would therefore be expected. The isotope

^{244}Cm , a major contributor to decay heat and important contributor to the radiation source term for spent fuel, is predicted within 9% of the measured data. The other measured curium isotopes are consistently underpredicted, with about 6 to 37%, depending on the specific nuclide and measured sample.

Results for cesium isotopes are illustrated in Fig. 4. The ^{133}Cs isotope, an important fission product in determining the reactivity of spent fuel (burnup credit), is overestimated by about 4%. As expected, ^{137}Cs , a major gamma source, is very well predicted. The ^{134}Cs nuclide, produced mainly by neutron capture in ^{133}Cs and important to decay heat and gamma sources at short cooling times, is underestimated by 12 to 15%. This underestimation is consistent with benchmark results obtained for other samples (Hermann et al., 1996) and is likely due to uncertainties in the evaluated cross section data used for depletion simulations.

Lanthanides results are illustrated in Fig. 4 for neodymium and cerium nuclides and in Fig. 5 for promethium, samarium, europium, and gadolinium isotopes. With the exception of ^{142}Nd for sample L2, all neodymium nuclides are predicted within 5% of the measurement. The ^{149}Sm isotope, which is one of the most important fission products for burnup credit criticality calculations, is overestimated by 9 to 15%, depending on the sample. The ^{147}Sm and ^{148}Sm nuclides are underestimated in all samples, by about 12 and 21%, respectively; whereas, ^{151}Sm and ^{152}Sm are consistently overestimated in the range 20 to 30%; ^{150}Sm and ^{154}Sm are better predicted, within 5 and 7% of the measurement. The nuclides ^{153}Eu , important for burnup credit criticality calculations, and ^{154}Eu , an important gamma emitter, are predicted within 9 and 11% of the experiment. The ^{155}Eu nuclide and decay daughter ^{155}Gd nuclide are both consistently underestimated in the range 23 to 39%. The isotope ^{147}Pm is estimated within 13% of the measurement.

The results for metallic fission products are illustrated in Fig. 6. The isotope ^{90}Sr and its progeny ^{90}Y are dominant fission products of importance to decay heat applications; ^{90}Sr is underestimated by less than 2% for samples H and L1 and by about 12% for sample L2; its underestimation for each of the samples is comparable to the reported experimental uncertainty. The ^{95}Mo , ^{99}Tc , ^{101}Ru , and ^{103}Rh nuclides, all important in burnup credit applications that include fission products, are predicted within 9, 19, 13, and 7% of the measured data, respectively; ^{109}Ag , minor fission product in

burnup credit, is very well predicted for sample L2 but highly over-predicted, by more than 100%, for the other two samples. The discrepancy and high variability between the results for similar samples indicates difficulties in measuring ^{109}Ag , likely associated with incomplete recovery in the solution and therefore under-reporting for some measurements. The other measured metallic fission products, ^{106}Ru and ^{125}Sb , both gamma emitters important to source term calculations, are predicted within about 8 and 64%, respectively. Note that overall there is a better agreement of the calculation and measurement for the metallic products in sample L2 measured at laboratory C than for the other two samples measured. It is known that the metallic fission products are very difficult to measure as they may not be completely recovered from the dissolved fuel.

When assessing the level of agreement between calculation and experiment, one needs to consider the experimental errors as well as other problems or limitations related to measurement or data required for simulations. Both the uncertainty in the data used to build the computational model and the measurement uncertainty are manifested in the observed code bias, and there is no prescription on how to isolate and quantify the sources of such uncertainties. The isotopic radiochemical measurement is a very complex process with a highly elaborate methodology that may include not only the mass spectrometric analysis, but also many other steps, such as dissolution of the sample to obtain a solution to be used for analyses, chemical separations of elements from the solution before measuring the isotopic content of those elements through a spectrometric method, spiking, dilution, etc. Even though isotopes of different elements are measured using the same spectrometric technique, the problems that can occur in the measurement process and the associated uncertainties may vary from element to element and from isotope to isotope.

6. Conclusion

The isotopic measurement data analyzed in this paper represent a valuable addition to the set of spent fuel experimental data currently available for code validation, enabling the evaluation of isotopic bias and uncertainties in high burnup spent fuel calculations. The use of independent measurements

and cross check to reduce uncertainties in experimental data gives high confidence in the reliability and accuracy of the measurement data from the MALIBU program. The measurements include extensive isotopic data for the actinides and fission products of high importance to spent fuel safety applications, including burnup credit, decay heat, and radiation source terms.

This set of measurement data was used to validate the isotopic depletion and neutronic solutions of the TRITON depletion sequence of the SCALE computer code system. The agreement between calculation and measurement is generally good and consistent with results obtained from previous evaluations of experimental data obtained from different programs for lower burnup fuel.

As for any other depletion tool, the accuracy of the TRITON predictions for the isotopic concentrations is highly dependent on the quality of the cross section and nuclear data used in the calculation. As previously mentioned, the calculations presented in this paper were based on cross sections obtained from ENDF/B-V data files, and the resonance self-shielding treatment was based on the NITAWL module in SCALE. Work is in progress to redo the analysis using recently developed cross sections based on ENDF/B-VII data and using for self-shielding the CENTRM/PMC methodology available in SCALE. Preliminary results are encouraging, showing significant improvements with respect to the prediction of many of the fission products. Notable are samarium, europium, and gadolinium isotopes, some of them important for burnup credit and criticality safety applications that credit fission products, for which the agreement between the calculated and measured data is within 10%. Also, a large improvement is seen in the prediction of ^{134}Cs , an important contributor to decay heat at a short cooling time; this isotope is predicted within a few percent of the measurement when using cross sections based on ENDF/B-VII data.

The work discussed in this paper is part of a larger effort at ORNL to document and evaluate high-quality radiochemical assay data for a wide range of pressurized and boiling water reactor fuel designs. The purpose of this effort is to compile, from domestic and international programs, a large experimental database of isotopic data for the actinides and fission products of importance to spent fuel safety applications, in order to enable the evaluation of isotopic bias and uncertainties in spent fuel calculations. These data are to be applied to

validate the TRITON depletion analysis sequence of the SCALE computer code system.

Acknowledgement

The authors would like to thank the U.S. Nuclear Regulatory Commission, Office of Nuclear Regulatory Research, for sponsoring this work.

References

- Boulanger, D., et al., 2004. High burnup PWR and BWR MOX fuel performance: a review of Belgonucleaire recent experimental programs. CD Proceedings of the 2004 International Meeting on LWR Fuel Performance, Orlando, Florida, USA.
- Goodall, P., and Johnson, S.G., 1997. High-resolution inductively coupled plasma atomic emission spectrometry for the determination of burnup in spent nuclear fuel, *Appl. Spectroscopy* 51(2).
- Haar, L., Gallagher, J.S., and Kell, G.S., 1984. NBS/NRC steam tables: thermodynamic and transport properties and computer programs for vapor and liquid states of water in SI units, Taylor & Francis, Levittown, PA.
- Hermann, O.W., Bowman, S.M., Brady, M.C., and Parks, C.V., 1996. Validation of the SCALE system for PWR spent fuel isotopic composition analyses, ORNL/TM-12667, Oak Ridge National Laboratory.
- de Kruijf, W.J.M. and Janssen, A.W., 1996. The effective fuel temperature to be used for calculating resonance absorption in a $^{238}\text{UO}_2$ lump with a nonuniform temperature profile, *Nucl. Sci. Eng.* 123, 121–135.
- MALIBU Program, 2004. Radiochemical analysis of MOX and UOX LWR fuels irradiated to high burnup. Technical proposal MA2001/02, Belgonucleaire, Brussels, Belgium.
- SCALE 5.1, 2006. SCALE: A modular code system for performing standardized computer analyses for licensing evaluations, ORNL/TM-2005/39, Version 5.1, Vols. I–III. Available from Radiation Safety Information Computational Center at ORNL as CCC-732.