

Burnup Calculations and Chemical Analysis of Irradiated Fuel Samples Studied in LWR-PROTEUS Phase II

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Abstract

The isotopic compositions of 5 UO₂ samples irradiated in a Swiss PWR power plant, which were investigated in the LWR-PROTEUS Phase II programme, were calculated using the CASMO-4 and BOXER assembly codes. The burnups of the samples range from 50 to 90 MWd/kg. The results for a large number of actinide and fission product nuclides were compared to those of chemical analyses performed using a combination of chromatographic separation and mass spectrometry. A good agreement of calculated and measured concentrations is found for many of the nuclides investigated with both codes. The concentrations of the Pu isotopes are mostly predicted within $\pm 10\%$, the two codes giving quite different results, except for ²⁴²Pu. Relatively significant deviations are found for some isotopes of Cs and Sm, and large discrepancies are observed for Eu and Gd. The overall quality of the predictions by the two codes is comparable, and the deviations from the experimental data do not generally increase with burnup.

KEYWORDS: *Burnup calculations, post-irradiation examinations, isotopic concentrations, assembly codes, high burnup*

1. Introduction

Samples from highly-burnt fuel rods irradiated in Swiss PWR and BWR power plants were investigated in the Phase II of the LWR-PROTEUS project [1]. This programme has been carried out in a cooperation between the Swiss nuclear utilities and Paul Scherrer Institute (PSI), aiming at extending the validation of core design calculational tools and thus facilitating the introduction of more efficient and more flexible fuel management strategies. The reactivity worths of pieces cut from the rods were measured in a typical PWR test zone in the PROTEUS zero-power research reactor, and small samples from adjacent locations of the same rods were dissolved and chemically analyzed for 17 actinide and 40 fission product nuclides in the PSI hot laboratory. A total of 13 samples, 11 of which came from a PWR (7 UO₂, 4 MOX) and 2 from a BWR, were included in the experimental programme. This paper describes the burnup calculations performed using the assembly codes CASMO-4 and BOXER and the comparison of the isotopic inventories with the results of the chemical assays for 5 PWR UO₂ samples with high burnups. Calculations for the remaining samples as well as chemical analyses for some of the samples are still in progress.

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2. Description of the Samples

The samples considered here were cut from UO₂ fuel rods from a Swiss PWR with burnups ranging from ~50 MWd/kg to ~90 MWd/kg. The rods investigated were taken from various radial positions within the fuel assemblies. Axially, the 40 cm long samples for the reactivity worth measurements were selected from the middle part of the rods in which the axial burnup distribution is practically flat (minimum 0.6 m, for most of the samples ≥ 1 m from the ends of the active fuel column), avoiding the parts affected by the presence of spacers. The samples for the chemical assays were cut from axial locations adjacent to one of the ends of these pieces. All the rods chosen for PIE had an initial enrichment of 3.5 wt-% ²³⁵U and were irradiated for 3 to 7 12-month cycles. The “overburnt” rods with 5 or more cycles irradiation time remained in their original assemblies for 4 cycles, after which they were relocated (up to 3 times) to different assemblies which themselves already had rather high burnups.

3. Chemical Analyses

3.1 Sample Preparation

The irradiated fuel samples were dissolved using a HNO₃/HCl (Merck, Suprapur) mixture in a high pressure digestion equipment (Berghof, Germany) at 170 °C for 3 h. Stock solutions were prepared by dilution with 1 M HNO₃ up to a concentration of about 0.5 mg fuel/g solution.

3.2 Instrumentation

The chemical analyses were performed using an online combination of high performance liquid chromatography (HPLC) and a multicollector inductively coupled plasma mass spectrometer (MC-ICP-MS) [2]. A DX-600 GS50 HPLC system (Dionex, Switzerland) equipped with a CG5A guard and a CS5A analytical column (2 mm × 250 mm) and a 25 μ l injection loop was coupled to the Neptune MC-ICP-MS (ThermoElectron, Germany). The CG5A and CS5A columns are filled with a mixed-bed ion-exchange resin with both anion and cation exchange capacity. The flow rate of the HPLC system was 0.25 ml·min⁻¹. The isotope ratio measurements on the transient HPLC signals were performed in the static, low-resolution mode of the MC-ICP-MS with an integration time of 1.049 s per data point. The mass discrimination was corrected using reference materials for each of the measured elements. Isotope dilution analyses (IDA) were used in order to quantify the concentrations of the elements in the fuel samples. Among other advantages, IDA is quite insensitive to loss of sample during matrix separation on the chromatographic column. For IDA, aliquots of the stock solutions were mixed with spike isotopic reference materials of the corresponding elements. Non-spiked aliquots were directly analyzed for the determination of the isotopic composition of the elements. Typical uncertainties of the isotopic composition of the elements are <0.1%, whereas the uncertainty of the elemental concentrations is in the range of 1–3%. These combined uncertainties are mainly influenced by the quality of the spike material and the concentration of fuel in the solutions.

3.3 Burnup Measurements

The burnup of the fuel was determined using ¹⁴⁸Nd as the burnup monitor. The fission yields for ¹⁴⁸Nd used in the processing of chemical results to burnups are averages of the values for the four main fissionable nuclides weighted with the calculated contributions of these nuclides to accumulated fissions in the samples. The measured burnups have an uncertainty of approximately 2.5%, the dominant contribution being that of the basic fission yield data used.

4. Calculations

4.1 Irradiation Histories

Irradiation histories of the samples which are needed as input data to the burnup calculations were provided by the fuel vendor based on the results of a nodal core simulator with pin power reconstruction. The power and the burnup of the samples as well as the calculated values of moderator and fuel temperatures and boron concentration are given at a few time points per cycle. These data are subject to typical uncertainties of nodal reactor calculations, which in turn have some effect on the calculated isotopic concentrations that cannot be easily quantified and depends strongly on the nuclide. A somewhat larger uncertainty than usual must be expected for the burnups of the samples relocated to different host assemblies due to the approximations used in the calculations for the tracking of these rods, particularly in cases where the active length of the new host assembly was different from that of the relocated rod. The comparison of the calculated sample burnups with the measured values (see above) shows a quite good agreement. The calculated burnups are 1–5% less than the experimental data, but for the majority of the samples the deviation is within the uncertainty of the measured values.

4.2 Codes and Models used

Burnup calculations were performed using the CASMO-4 [3] and BOXER [4] fuel assembly codes. CASMO-4 is a widely-used assembly code developed by Studsvik Scandpower, Inc. One of its main features is the characteristics method used for the two-dimensional transport calculations, which allows a detailed representation of the fuel assembly without using pin cell homogenization. Version 2.05.10 of the code was used in conjunction with the J2LIB cross section library based on JEF-2.2 nuclear data. BOXER is an assembly code developed at PSI. It is characterized, amongst other things, by a resonance self-shielding calculation in a large number of energy points (typically 7000–8000 points between 1.3 and 900 eV) and by a transmission probability 2-D integral transport method for homogenized cells. The BOXER library is based on the JEF-1 evaluation, but with fission product yields from JEF-2.2.

Models of the fuel assemblies from which the sample rods were extracted were used for all the calculations, thus taking into account the effects of the actual surroundings (particularly the presence of guide tubes) on the neutron spectrum in the samples. The variation of sample power, boron concentration and fuel and moderator temperature was followed in a few steps per cycle, using in each step the average of the values given at its beginning and its end. The histories of the relocated samples were followed in detail: the sample was depleted in the original assembly to the burnup at the end of the last cycle before relocation. In parallel, the receiving assembly was depleted to the node-average burnup at this time point at the axial position of the sample using typical values of the state parameters. Then, at the time of the relocation, the calculated composition of the sample was assigned to its location in the new host assembly for the following cycle, and the calculation for the reconstituted assembly was continued up to discharge of the sample or to the next relocation.

In BOXER, it was possible to perform the assembly depletion calculations to a specified burnup value in the sample rod. In CASMO-4, the assembly-average burnup had to be adjusted iteratively such as to match the given sample burnup. Two iterations were sufficient to get a very close agreement. Burnup steps of ≤ 1 MWd/kg were used in accordance with ARIANE analyses performed at PSI [5], with shorter steps after each change of the irradiation conditions (power, temperatures, boron concentration) to burn in the new equilibrium densities of short-lived nuclides. The decay of radioactive nuclides was followed explicitly both in

the refuelling intervals between the cycles and from discharge of the samples to the time of the chemical measurements for each element. The default 8 energy-group structure was used in the CASMO-4 calculations. For BOXER, an optimized 15-group structure with rather fine groups in the thermal energy range and around the 1 eV resonance of ^{240}Pu was used. This same group structure was found to give a good agreement of nuclide inventories with calculations using the full library structure also for MOX fuel.

4.3 Sensitivity Studies

The sensitivity of the calculated nuclide concentrations to the following calculational options was studied: burnup steps, radial subdivision of the fuel pellets and a separate treatment of the sample for the cell calculations. The latter treatment means that the pin-cell spectrum is calculated for the actual sample composition rather than an assembly-averaged composition and, in the case of BOXER, that the Dancoff factor is determined for the sample with its actual surroundings (CASMO-4 automatically computes a separate value of the Dancoff factor for each pin). The results for U, Pu and the major fission products differ by mostly less than 1% between the different calculations. An increase or reduction of the burnup steps to 0.5 or 2 MWd/kg had very little effect on all nuclides investigated (the 1 MWd/kg steps used are of course already very short). The densities of higher actinides, particularly curium, were found to be more sensitive to the radial mesh in the fuel and to the Dancoff treatment. Refinements of these options produced differences up to 3 or 4%. For the radial subdivision of the fuel, the results obtained using 4 or 10 equivolumic zones were almost identical. For the cell calculations, the dominant effect in BOXER was shown to be that of the Dancoff factor. The effect of using the actual composition in the cell calculation for non-relocated samples is minor in both codes. The relatively high sensitivity of Cm concentrations to these options can be explained qualitatively by the fact that many reaction steps are involved in the formation of Cm from U, and these reactions appear to be affected in a similar way, or at least in the same direction, by the changes investigated.

Nevertheless, the default options, i.e. one radial zone in the fuel and a common treatment for all pin cells (except for relocated samples), which are representative of production-type calculations, were retained for the burnup calculations presented here. When comparing calculated and measured Cm concentrations, one should however be aware that these results are rather sensitive to the calculational options mentioned (and also to the burnup, because their densities increase with a high power of the burnup) and that the nuclear data used may not be the only cause of observed differences.

5. Comparison of Calculated and Measured Results

In this section, the differences between the calculated (C) and experimental (E) nuclide concentrations in the samples are discussed. In these comparisons one has to keep in mind that the calculations were carried out to the burnup values obtained from the fuel vendor, which are a few percent less than the measured values for some of the samples. This difference in burnup may cause an apparent negative C–E deviation in those samples for nuclides whose concentrations vary strongly with burnup.

In the following figures, error bars include a contribution for observed differences between the fuel concentration in the analyzed solutions (by which the measured nuclide concentrations were divided to obtain the values in mg per g of fuel) determined by weighing of the samples and that derived from the measured elemental concentrations. These differences reach up to

3% in some of the samples. For this reason, the errors appear to be varying strongly from one sample to another. It is expected that this uncertainty could be reduced by computing the nuclide concentrations relative to the fuel concentration determined by the latter of the methods mentioned above (this would also shift the results for all nuclides in a particular sample by the same percentage). This has, however, not yet been done.

5.1 Actinides

Figure 1 shows the relative differences between the calculated concentrations of the main uranium and plutonium isotopes and the measured values. When looking at the deviations for ^{235}U , one has to bear in mind that the abundance of this nuclide in the highly-burnt samples (with 3.5 wt-% initial enrichment) is very low. The systematically higher concentration of this nuclide in the BOXER results appears to be consistent with the differences found for ^{239}Pu (see below): BOXER predicts a higher plutonium concentration than CASMO-4 and consequently a lower ^{235}U contribution to total fissions. The ^{236}U concentration is underpredicted by both codes, with an average deviation of approximately 6% in CASMO-4 and some 2% in BOXER. The CASMO-4 results agree qualitatively with the findings of French investigations using JEF-2.2 nuclear data [6], but the difference is slightly more pronounced in our results.

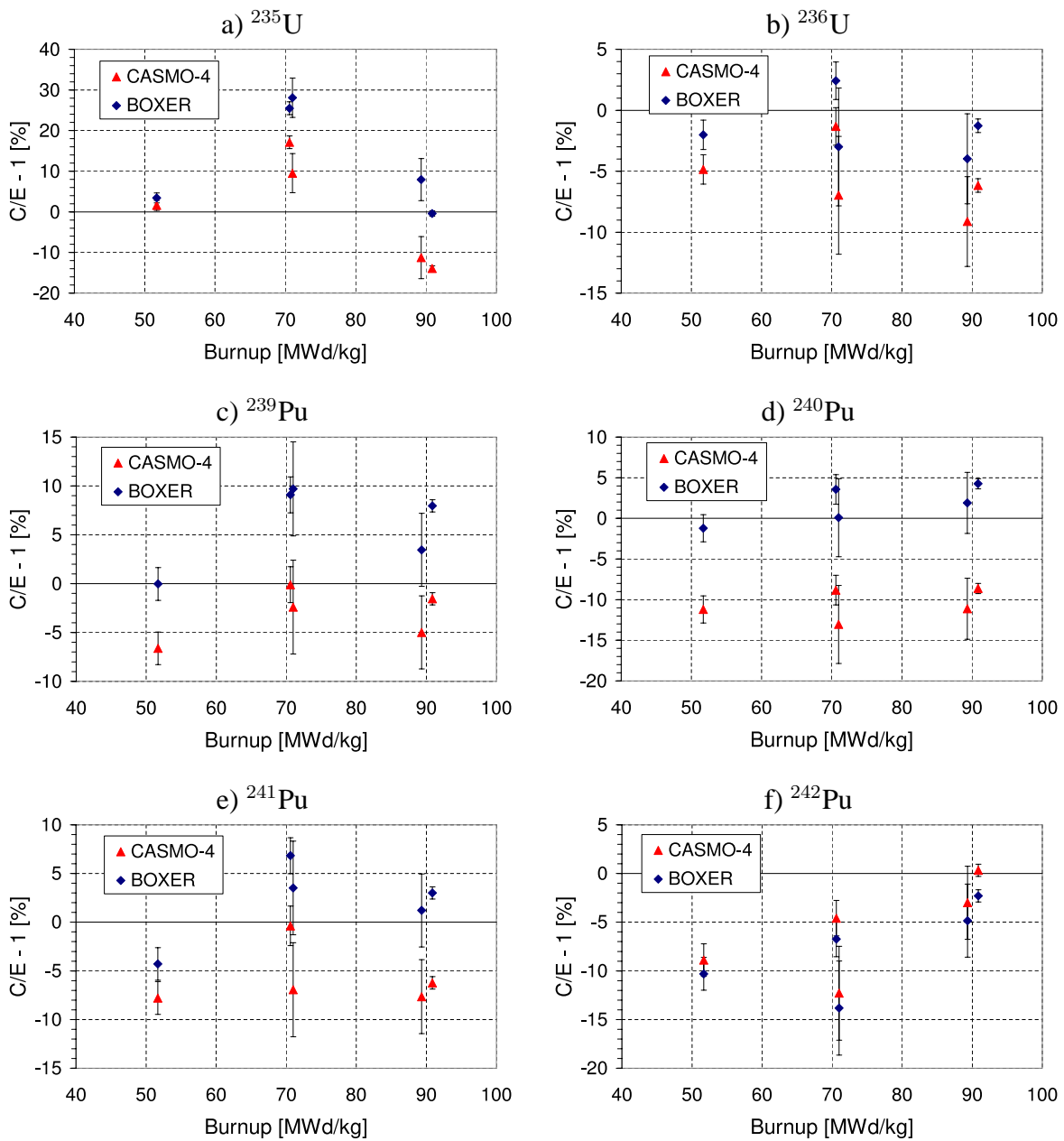
The differences of the CASMO-4 and BOXER results for ^{239}Pu , ^{240}Pu and ^{241}Pu are quite striking, whereas the concentration of ^{242}Pu is underpredicted to practically the same amount by the two codes. The comparison of the C–E deviations for the different isotopes indicates that there are some differences between the calculated and measured Pu isotopic vectors. For ^{239}Pu BOXER computes systematically higher concentrations than CASMO-4, the difference ranging from 6 to 12% with a trend to increase with higher burnup. This difference looks relatively large, considering that ^{239}Pu is the most important fissile nuclide in highly-burnt fuel. The comparison with the chemical assays shows that CASMO-4 underpredicts the concentration of ^{239}Pu by a few percent and BOXER overpredicts this quantity to a somewhat larger extent. The results for ^{241}Pu are qualitatively similar to those for ^{239}Pu , but with a quite systematic underprediction by $\sim 7\%$ (except for one sample) by CASMO-4 and a less positive deviation (2–6%) than for the latter isotope in the case of BOXER. The ^{240}Pu content of the burnt fuel samples is systematically underestimated by some 10% in the CASMO-4 calculations and somewhat overestimated by BOXER.

The concentration of curium is quite significantly underpredicted by both CASMO-4 and BOXER, the deviations for the two codes being similar. The calculational results for ^{244}Cm and ^{245}Cm are approximately 20% lower than the measured values, and those for ^{246}Cm are lower by $\sim 30\%$. These differences are clearly larger than those expected on the basis of the observed sensitivity of Cm concentrations to calculational options (see above) or due to inaccuracies of the calculated sample burnups.

5.2 Fission Products

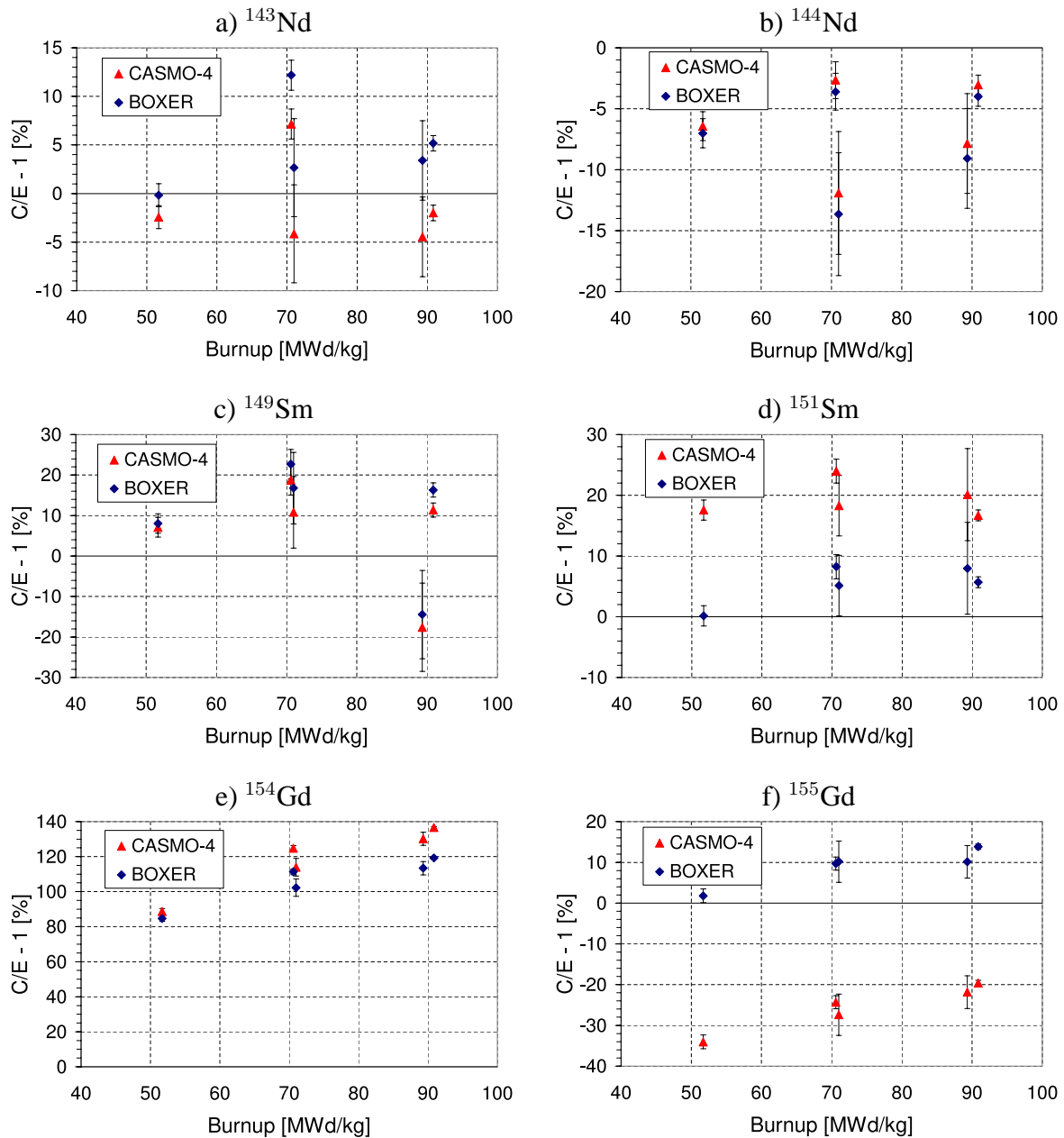
The deviations of the calculated concentrations of some important isotopes of Nd, Sm and Gd from the experimental data are shown in Figure 2, and those for Cs and some metallic fission products in Figure 3. The concentrations of ^{143}Nd are close to the measured values (except in one sample), with a slight underprediction (2–4%) by CASMO-4 and a small overprediction (up to 5%) by BOXER. In contrast to this, the concentration of ^{144}Nd is systematically underestimated by a few percent, the two codes giving very similar results (the $>10\%$ underprediction for one of the 70 MWd/kg sample appears to be linked to an underestimate of the burnup).

Figure 1: Deviations of calculated actinide concentrations from the measured values (in %).



The concentration of ^{149}Sm is clearly overpredicted by up to $\sim 20\%$, except for one sample for which the experimental uncertainty is much larger than for the others. The concentration of this nuclide has been found to be quite sensitive to the modelling of the irradiation history, particularly the power history near the end of the last cycle (due to the buildup by decay of short-lived ^{149}Pm after discharge). It is possible, therefore, that the simulation of the parameter history by only a few steps per cycle contributes to some extent to the overprediction of the ^{149}Sm concentration. For ^{151}Sm , the CASMO-4 results are some 20% too high and those of BOXER $\sim 7\%$. The deviations of the CASMO-4 results for ^{152}Sm are similar to those for ^{151}Sm , whereas the BOXER results are in close agreement with the measured values.

Figure 2: Deviations of calculated concentrations for Nd, Sm and Gd from the measured values (in %).

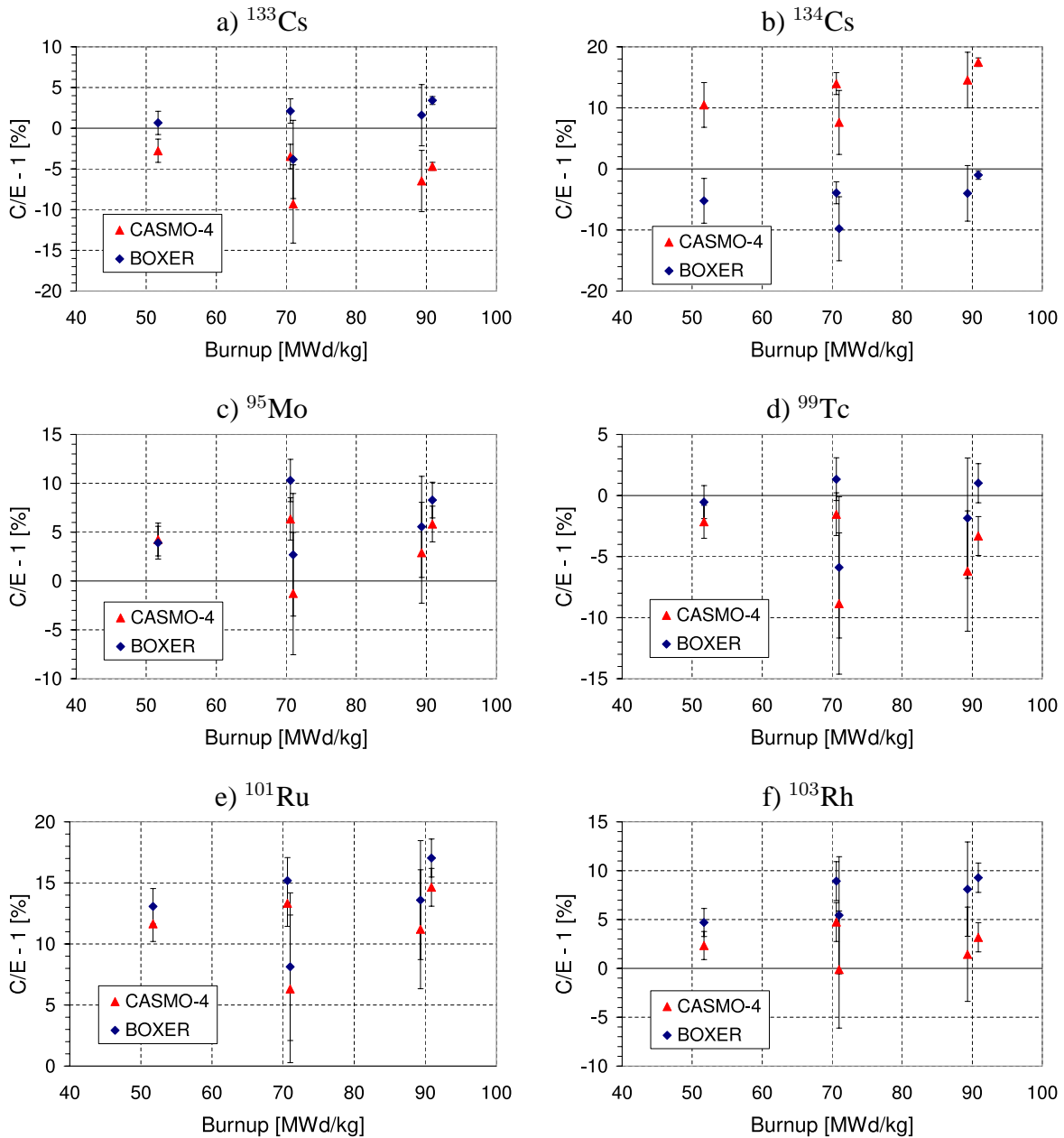


Larger deviations from the measured concentrations are found for Eu and Gd. These are illustrated for ^{154}Gd and ^{155}Gd in Figure 2 e) and f). The deviations for ^{154}Eu and ^{155}Eu are consistent with those for the corresponding Gd isobars. The concentration of ^{154}Gd is over-predicted by approximately a factor of 2 by both CASMO-4 and BOXER. For ^{155}Gd , however, the results of the two codes differ significantly: The results of CASMO-4 are 20–30% low and those of BOXER typically $\sim 10\%$ high. The findings for mass number 154 agree with those of comparisons of calculations using JEF-2.2 nuclear data against PIE carried out in France [6]. In Refs. 6 and 7 it was shown that important resonances are missing in the JEF-2.2 evaluation for ^{154}Eu and that the results for this isotope can be significantly improved by using cross sec-

tions from the latest ENDF/B-VI releases. For ^{155}Gd , however, the CASMO-4 results are not consistent with those of the French investigations, the latter having found an overestimate of the order of 10%.

The results of CASMO-4 and BOXER for the concentrations of fission products with weak neutron absorption, such as ^{90}Sr , ^{137}Cs , ^{144}Nd , ^{146}Nd , ^{150}Nd , ^{148}Sm and ^{154}Sm , are very close to each other (within $\sim 1\%$). This may be due to the fact that the fission yields used in the two libraries come from the same source, viz. JEF-2.2. The calculated concentrations from both codes for ^{90}Sr , ^{137}Cs and ^{150}Nd also agree with the experimental data within a few percent. The same is true for the more absorbing fission products ^{99}Tc and ^{145}Nd .

Figure 3: Deviations of calculated concentrations for Cs and metallic fission products from the measured values (in %).



For ^{133}Cs and ^{134}Cs , the trends for the two codes are different: The concentration of ^{133}Cs is slightly overpredicted by BOXER and underpredicted to a somewhat larger amount by CASMO-4. For ^{134}Cs , on the other hand, the CASMO-4 results are more than 10% too high and those of BOXER are low by an average of $\sim 5\%$. These differences might be explained by an overestimate of the neutron capture in ^{133}Cs by CASMO-4, because ^{134}Cs is mostly produced by this reaction. The French studies actually suggest that this cross section is too high in JEF-2.2, particularly for the first strong resonance at ~ 6 eV [7]. However, the resonance self-shielding of ^{133}Cs and the overlap with the 6.7 eV resonance of ^{238}U may also play a role, particularly at high burnups. ^{133}Cs is included in the pointwise resonance calculation in BOXER, but in CASMO-4 it is not self-shielded. It is also to be noted that the deviations from the measurements of the CASMO-4 results for ^{133}Cs are consistent with the French results [6], but this is not the case for ^{134}Cs .

The concentrations of the metallic fission products ^{95}Mo , ^{101}Ru and ^{103}Rh are generally overpredicted, but to varying extents: The results of the two codes for ^{95}Mo and ^{101}Ru are similar, with an overprediction by approximately 5% for the former nuclide and some 12% for the latter (the apparent “outlier” at ~ 70 MWd/kg seems to be due to an underestimate of the burnup). For ^{103}Rh the CASMO-4 results are in the average some 3%, those of BOXER $\sim 7\%$ higher than the experimental values.

6. Conclusions

The isotopic compositions of 5 UO_2 samples from a Swiss PWR with burnups ranging from 50 to 90 MWd/kg have been calculated using the CASMO-4 (using a JEF-2.2 library) and BOXER (with JEF-1 nuclear data) codes and compared to the results of chemical analyses. Overall, a satisfactory agreement of the calculated and measured concentrations has been found. The quality of the predictions by CASMO-4/JEF-2.2 and BOXER/JEF-1 is globally comparable, the number of nuclides for which the results of one code agree better with the experimental values than those of the other being about equal. Some of the systematic and relatively significant trends coincide with those found in other investigations using the same basic nuclear data. Unfortunately, libraries based on the JEFF-3.0 or JEFF-3.1 evaluations are not available for the codes used here. The burnups of the samples investigated in the present work extend far beyond the range for which PIE has normally been performed previously. In this context, it is interesting to note that the differences between the calculated and measured concentrations for most of the nuclides are fairly constant in the burnup range investigated and there is generally no indication for a trend of increasing deviations with burnup.

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