Destructive radiochemical burn-up determination at SCK•CEN using isotopes of Cs, Ce and Nd as fission product monitors

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Abstract

At SCK•CEN, the fission product monitors selected for destructive burn-up determination are stable Nd-isotopes and the γ-emitters ^{137}Cs and ^{144}Ce. These two groups of fission products are analyzed with a different analysis procedure, i.e. the Nd-isotopes are measured by isotope dilution mass spectrometry on a TIMS instrument after a complex sample separation procedure, whilst the γ-emitters are measured directly on a diluted spent fuel solution by γ-spectrometry. Different types of irradiated industrial and experimental nuclear fuels were treated in the chemical hot cells for radiochemical burn-up analyses The dissolution and analysis procedures applied, in combination with an optimized sampling method for spent fuel samples, resulted in an excellent agreement between the FIMA values derived from the different fission product monitors for fuels having a burn-up in the range 20 to 80 GWd/tM.

Keywords: Nuclear fuels, burn-up, actinide, fission product, FIMA, radiochemistry, TIMS, spectrometry

1. Introduction

The burn-up of irradiated nuclear fuels is one of the most important parameters in the field of reactor fuel management, fuel development, fuel performance and fuel safety and criticality related to spent fuel manipulation and safeguards. Although neutron-physics calculation codes and non-destructive assay methods for burn-up determination have been developed over the last 30 years, neither of these approaches can achieve the low uncertainties that are associated with a radiochemical procedure. As a result, destructive radiochemical and chemical analysis is still the established reference method for an accurate and reliable burn-up determination in present day commercial and experimental spent nuclear fuels.

Destructive methods are based on the analysis of the building up of prominent actinide activation products and of selected fission product monitors in the fuel. As a result, in radiochemistry, burn-up is usually defined as atom percent fissions or ' **F**issions per **I**nitial heavy **M**etal **A**tom' (**FIMA)** rather than in terms of energy release. The resulting values for FIMA can easily be recalculated to GWd/tM using a conversion factor that is a function of the fuel type and the power reactor facility. Typically this value is 9.6 for a UO_2 and 9.9 for a MOX BWR fuel.

Several fission products formed during the irradiation of the fuel are potential burn-up monitors. At SCK•CEN the stable isotopes of Nd (^{143}Nd, ^{144}Nd, ^{145}Nd, ^{146}Nd, ^{148}Nd, ^{150}Nd) and two γ-emitting radionuclides ^{137}Cs ($t_{1/2}$ = 30.02 y) and ^{144}Ce ($t_{1/2}$ = 284.9 d) are selected for the (radio-)chemical analysis. These two groups of burn-up monitors are each analyzed by a different and completely independent measurement technique: Nd is analyzed, after separation, by thermal ionization mass spectrometry (TIMS), whilst ^{137}Cs and ^{144}Ce are analyzed directly on a diluted spent fuel solution by means of γ-spectrometry. This multiple approach provides a reliable cross-check on the %FIMA determination within the extensive and time-consuming analysis procedure. In this paper the radiochemical procedure applied for burn-up determination at SCK•CEN is summarized. A comparison of %FIMA values derived from the different burn-up monitors against ^{148}Nd, the ASTM procedure E321-69 proposed burn-up monitor, is presented.

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2. (Radio-)Chemical methodology for burn-up determination

2.1. Sampling

The radiochemical burn-up methodology starts with the sampling in a hot cell environment. The fuel sample is carefully chosen based on a non-destructive γ-scanning of the fuel rod or plate under investigation. For fuel rods made up with pellets, typically a sample of 3 pellets is cut. The cutting edge is chosen mid-pellet, as derived from the γ-scanning, thus resulting in a sample comprising two complete pellets, 2 half pellets and three pellet interfaces (fig-1). For HEU and LEU fuel plates with UAlx, U_3Si_2 or UMo, where the dispersion fuel is confined between aluminum plates, the sample size is likewise defined to manage the local 'micro' (i.e. sub mm) variations as revealed by the γ-scanning. This approach provides a good correlation between the radiochemistry results and both the n-physics calculations and γ-scanning results, as all can be related to the same 'bulk' material.
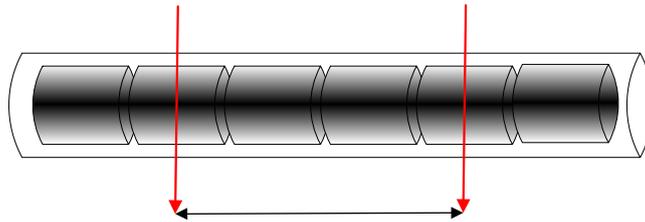

Fig. 1 - Cutting positions in a fuel rod sample for radiochemistry

2.2. Fuel dissolution

The fuel samples are dissolved in a two step procedure using successively nitric acid and a mixture of nitric and hydrofluoric acid, both kept at their boiling point. The dissolution procedure applied achieves dissolution of U, Pu, Am, Cm, Np, Nd, Cs and Ce with an efficiency of > 99.9%. For irradiated U- and U,Pu-Zr alloy fuels, the fuel matrix can be dissolved selectively thereby leaving the cladding intact. For irradiated U-Al fuels, where the dispersion fuel is confined as a thin wafer between aluminum plates, complete dissolution of the fuel is only possible by dissolving the Al (cladding and matrix) as well during the first step. In that case, dissolution of the aluminum is aided by the addition of catalytic amounts of mercury(II). The resulting spent fuel mother solution is diluted with 1 M nitric acid to a concentration of 0.4 to 0.5 g/L. From this dilution a small aliquot is transferred from the hot cell to the laboratory for radiochemical separation and analysis.

2.3. Chemical and radiochemical analyses

The isotopic composition and concentration of U, Pu and Nd in the dissolved fuel solution is determined by means of isotopic analysis mass spectrometry (IA-MS) and isotope dilution mass spectrometry (ID-MS) measurements using TIMS. For ID-MS, an aliquot corresponding to approximately 1 mg of spent fuel is spiked with a mixed U-Pu standard containing ^{242}Pu and ^{233}U and with ^{146}Nd. The Nd-spike is previously irradiated in the BR2 reactor at SCK•CEN resulting in the production of ^{147}Nd ($t_{1/2}$ = 10.98 d), a γ-emitter that is used as a tracer for Nd during the separations. The IA-MS and spiked ID-MS samples are subjected in parallel to the same 3-column separation procedure. In a first step uranium and plutonium, as U(VI) and Pu(IV), are fixed on a Dowex1 anion exchange resin allowing a selective separation of U and Pu from minor actinides and fission products. Cerium, which has isotopes that interfere with the neodymium measurement at masses 142 and 144, is removed onto a column packed with a mixture of PbO_2 and Dowex1 resin. Finally, on a third column packed with HDEHP-kieselguhr neodymium can be separated from other trivalent rare earth elements, minor actinides, mono- and divalent fission products by using a nitric acid gradient elution. Small fractions of the purified U, Pu and Nd obtained from the IA and ID separation procedure are loaded onto rhenium filaments and are measured according to a standard procedure on a calibrated TIMS instrument.

Radiochemical measurements are performed on the diluted spent fuel solutions and on the purified Pu-fractions. For γ-spectrometry, 3 different 5 ml ampoules with increasing concentrations of spent fuel are prepared and measured on 2 independent HPGe-detectors. Both detectors are calibrated versus 2 different mixed radionuclide standard sources, traceable to NPL and to NIST respectively. The activity concentrations of different γ-emitting radionuclides present in an irradiated fuel, such as ^{106}Ru, ^{125}Sb, ^{134}Cs, ^{137}Cs, ^{144}Ce, ^{154}Eu, ^{155}Eu and ^{241}Am, can be determined. In the case of burn-up determinations, only the results of ^{137}Cs, ^{144}Ce and ^{241}Am are used for calculation. For α-counting and α-spectrometry, weighed aliquots of diluted fuel or purified Pu fractions are evaporated onto a Ta-disc and measured against a ^{241}Am standard source. In the case of spent fuel this technique provides information on the activity concentration of ^{244}Cm and ^{242}Cm. In the case of purified Pu the ratio of ^{238}Pu/(^{239}Pu+^{240}Pu) is determined, which, in combination with the isotopic composition obtained from TIMS measurements, results in a value for ^{238}Pu.

2.4. Burn-up calculation

The experimental data obtained from radiochemistry is recalculated from the date of analysis to the end of irradiation (EOL), and burn-up values, expressed as %FIMA, are derived from the different selected fission product monitors, taking into account the following considerations. (1) In a thermal reactor spectrum, the cross-sections for (n,γ) capture of the Nd-isotopes ^{143}Nd and ^{145}Nd are relatively high. This results in a significant burnout of these isotopes and in the buildup of ^{144}Nd and ^{146}Nd. Therefore, the results of ^{143}Nd + ^{144}Nd and of ^{145}Nd + ^{146}Nd are summed for calculation. (2) The number of atoms of ^{144}Nd and ^{144}Ce at EOL are summed for the final calculation of %FIMA based on $^{143+144}$Nd. (3) Fuel samples that are irradiated in the BR2 research reactor at higher neutron fluxes need to be corrected for the buildup of ^{148}Nd due to the ^{147}Nd(n,γ)^{148}Nd reaction on short-lived ^{147}Nd. (4) The radioactive burn-up monitors ^{137}Cs and ^{144}Ce have to be corrected for in-pile decay during irradiation. To derive an accurate in-pile correction factor, access to the irradiation history of the fuel element is indispensable. In an ideal situation the irradiation history at the position of the fuel sample for radiochemistry is known. Due to its shorter half-life ^{144}Ce is much more sensitive to in-pile and out-pile corrections than is ^{137}Cs.

2.5. Material Balance calculation

Material balance calculations are performed to assess the overall quality of the destructive burn-up measurements. For fuel rods from thermal power reactors this is fairly straightforward and only the weight of the fuel that was dissolved in the hot cell for analysis, the determined number of heavy atoms and calculated number of fissions have to be considered. For fuel plates where the cladding is also dissolved, the aluminum concentration in the spent fuel solution also has to be determined and taken into consideration.

3. Results and discussions

Over a period of 3 years a total of 17 fuel samples from several international fuel research programs such as TOPGUN (licensing of high burn-up 9×9 BWR MOX fuel), GERONIMO (licensing of 9×9 BWR MOX fuel), REBUS (burn-up related criticality credit validation for spent UO_2 and MOX fuel), RJH-fuel (LEU research reactor fuel qualification), HIMOX (high Pu content MOX fuel qualification) and MALIBU (spent fuel source term validation) were subjected to the radiochemical burn-up analysis methodology described here.

One important parameter which forms the basis of good quality control on the applied methodology, starting with the dissolution in the hot cell up to the %FIMA calculation, is the material balance. It permits detection of possible hot cell and laboratory errors and uncertainties. Material balance calculations for the power reactor fuel samples ranged from 98 to 102% with an average value of 99.3% $\pm$ 0.6%, indicating a good overall quality for the entire analysis process.
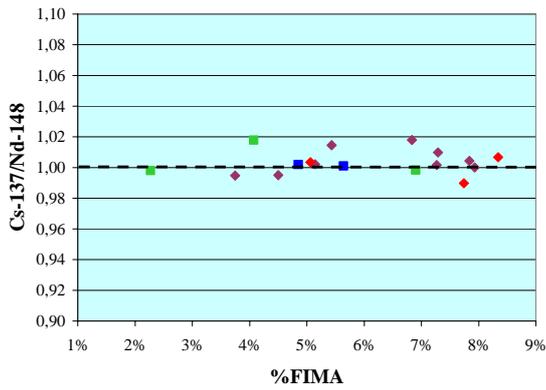
Fig. 2 %FIMA derived from ^{137}Cs versus ^{148}Nd

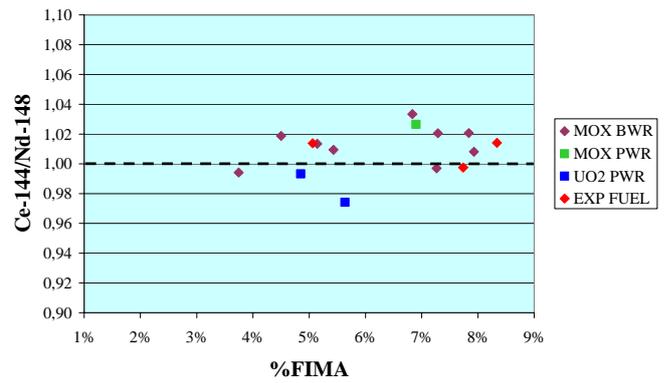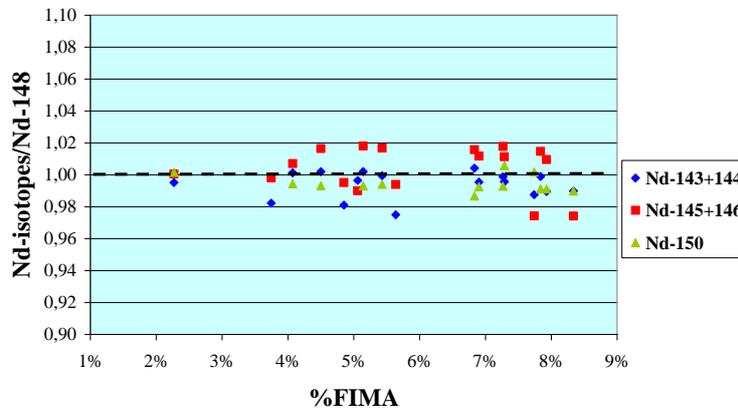**Fig. 3** %FIMA derived from ^{144}Ce versus ^{148}Nd

Fig. 3 %FIMA derived from $^{143+144}$Nd, $^{145+146}$Nd and ^{150}Nd versus ^{148}Nd

Figures 2, 3 and 4 show the ratios of %FIMA calculated from the different burn-up monitors ^{137}Cs, ^{144}Ce, $^{143+144}$Nd, $^{145+146}$Nd and ^{150}Nd versus the value calculated from ^{148}Nd. Excellent agreement was obtained for burn-up values derived independently, from ^{137}Cs and ^{144}Ce, and from different Nd-isotopes, in the range of 2 to 8 %FIMA ($\approx$ 20 to 80 GWd/tM) in a variety of present day PWR, BWR and research reactor fuels. Average ratios versus ^{148}Nd are (1.003 $\pm$ 0.004) for ^{137}Cs, (1.009 $\pm$ 0.008) for ^{144}Ce, (0.994 $\pm$ 0.004) for $^{143+144}$Nd, (1.004 $\pm$ 0.007) for $^{145+146}$Nd and (0.994 $\pm$ 0.003) for ^{150}Nd, indicating no significant bias in the applied approach.