MRS Advances

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Journal:	*MRS Advances*
Manuscript ID	MRSAdv-2017-0079.R1
Manuscript Type:	Regular Article
Date Submitted by the Author:	n/a
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Keywords:	actinide, nuclear materials, Pu, U, waste management

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Comparison of calculated and measured radionuclide inventory of a Zircaloy-4 cladding tube plenum section

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ABSTRACT

Cladding tubes of water-cooled nuclear reactors are usually made of Zircaloy and are an important retaining element for radionuclides present in the fuel both during predisposal activities such as reloading of fuel assemblies from interim storage casks to final disposal casks and during final disposal in the case of canister breaching. However, cladding integrity is affected by various processes during reactor operation and beyond, e.g. fuel cladding chemical interaction and fission product precipitation onto the inner cladding surface. Using experimental and modelling methods, the radionuclide inventory of an irradiated Zircaloy-4 plenum section is analyzed. Quantities of $^{235/238}$U, ^{237}Np, $^{238/239/240/241/242}$Pu, $^{241/243}$Am, $^{243/244}$Cm besides ^{14}C, ^{55}Fe, ^{125}Sb, ^{154}Eu, and $^{134/137}$Cs were (radio-)chemically determined in digested Zircaloy-4 subsamples. Measured inventories of activation products in the Zr-alloy are in good agreement with calculated values. However, amounts of actinides and fission products exceed the calculated inventory by factor ~57 (minor actinides and non-volatile fission products) and ~114 (^{137}Cs). Excess of minor actinides and part of enhanced Cs inventory originate from fuel residues deposited on the inner cladding surface during fuel rod fabrication, whereas vast amount of cesium is volatilized from subjacent fuel pellets and transported to the plenum.

INTRODUCTION

In Germany as well as many other countries, spent nuclear fuel (SNF) assemblies, after being discharged from a nuclear power reactor, are cooled in spent fuel pools for several years, and eventually sent for dry cask storage. Dual-purpose casks (CASTOR®, GNS) are used for transport and dry interim storage of SNF assemblies in facilities in Gorleben, Ahaus, and Nord, as well as on site of the nuclear power plants.

In the German waste management concept, SNF is designated for direct disposal in a deep geological repository available by 2050 at the best [1]. However, considering the delay in the site selection process so far as well as the time needed for exploration, construction, and commissioning of a repository for high-level waste, start of waste emplacement is expected by the end of this century/beginning of next century [1].

Thus, a prolonged dry interim storage of SNF assemblies is inevitable. Moreover, dry interim storage of SNF assemblies was intended to last only a few decades, and hence licenses for storing of CASTOR® casks in the interim storage facilities expires already in the years 2034 to 2047. Therefore, a thorough revaluation of all safety relevant aspects is required, taking into account the extended dry cask storage of SNF assemblies.

Integrity of the irradiated Zircaloy cladding after 50 to 100 years of dry interim storage is of importance e.g. to ensure a safe reloading of the fuel assemblies from the CASTOR® to the final disposal canister. However, the cladding is affected during reactor operation by various processes such as elongation of the fuel rods due to creep behavior and oxidation with the water coolant causing a reduction of the Zircaloy wall thickness, respectively. Further, dissolution and precipitation of hydrogen within the Zr-alloy matrix, during reactor operation, possibly leads to hydrogen embrittlement and delayed hydride cracking of the cladding. Swelling of the fuel pellets during irradiation due to fission products build-up eventually leads to the contact of the fuel pellets with the cladding. The so-called pellet/cladding interaction (PCI) induces tensile stress on the cladding, especially during power ramps. In presence of (volatile) fission (and activation) products released from the pellets stress-corrosion-cracking can occur.

Moreover, the radionuclide inventory of Zircaloy cladding is important for long-term safety assessments of SNF repositories since radionuclides present in the cladding are potentially released upon contact with ground water in a canister breach scenario.

Using experimental and modelling methods, the radionuclide inventory of an irradiated Zircaloy-4 plenum section is analyzed in this study. Although, there was not any fuel pellet present in the plenum during irradiation and storage, various actinides, fission and activation products are present at the inner surface of the plenum cladding. The results and findings of this study is prerequisite work for investigations on fuel cladding chemical interactions involving Zircaloy-4 cladding in contact with fuel pellets.

MATERIALS AND IRRADIATION CHARACTERISTICS

The studied Zircaloy-4 plenum cladding was sampled from fuel rod segment N0204 of fuel rod SBS1108. The fuel rod was irradiated during four cycles in the pressurize water reactor Gösgen (KKG, Switzerland) and discharged in May 1989 after 1226 effective full power days. During reactor operation, an average burn-up of 50.4 GWd/t_{HM} as well as average linear power of 260 W/cm was achieved.

EXPERIMENTAL AND ANALYTICAL METHODS

Subsamples of the Zircaloy-4 plenum section (see figure 1a) were dry cut using an IsoMet® Low Speed Saw (11-1180, Buehler Ltd.) equipped with an IsoMet® diamond wafering blade (11-4254, Buehler Ltd.). Cutting was performed very slow (about one hour per sample) to prevent overheating of the material. In total six subsamples (see figure 1b) with masses ranging from 119.7 ± 0.2 mg to 189.0 ± 0.2 mg were prepared by remote handling in a shielded box for dissolution experiments. Masses and dose rates were measured using an analytical balance (MS304S, Mettler-Toledo International Inc.) and a dose rate meter (6150AD6, automess – Automation und Messtechnik GmbH). Dose rate of the subsamples was typically less than 0.3 mSv/h.

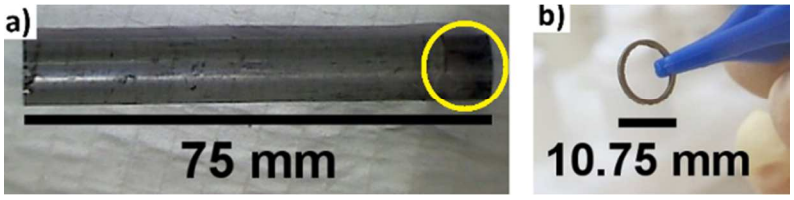

Figure 1. Pictures of the irradiated plenum Zircaloy-4 cladding: (a) dimensions, the yellow circle indicates the welded end-plug; (b) a subsample prepared for a dissolution experiment.

The specimens were digested within 30 minutes in a dilute H_2SO_4/HF mixture at room temperature and anoxic conditions using a flask or autoclave.

Radionuclides present in the digestion liquor (and gas phase) were analyzed using various analytical and separation methods.

α-spectroscopy was used to quantify $^{235,238}U$, ^{237}Np, $^{238,239,240,242}Pu$, $^{241,243}Am$, and $^{243,244}Cm$ (ion implanted Si semiconductor detector, MXR Model 1520, MCA System 100, ASP data evaluation software, Canberra Industries Inc.). Drops of a diluted (1:100) aliquot of the digestion liquor were placed on a metal disk (target) and dried for the measurements. α-spectroscopy was also performed from Pu isotopes after separation from other α-emitting radionuclides.

Fission products and minor actinides with characteristic γ-rays e.g. $^{134,137}Cs$, $^{241,243}Am$, ^{154}Eu, and ^{125}Sb were quantified in digestion liquors obtained from dissolution experiments performed with irradiated Zircaloy-4 using γ-spectroscopy. Measurements in this study were performed by means of an extended range coaxial Ge detector (GX3018, Canberra Industries Inc.) with a relative efficiency of ≥ 30%. Energy and efficiency calibration of the detector was performed using a certified multi-nuclide standard solution (Mixed Gamma 7600, Eckert & Ziegler Strahlen- und Medizintechnik AG). Data evaluation was performed using the Genie 2000 software (Canberra Industries Inc.). Aliquots of one milliliter from the digestion liquors were measured using APEX® screw-cap microcentrifuge tubes (2 mL, polypropylene, PP, Alpha Laboratories Ltd.).

Minor actinides, activation and fission products such as ^{14}C, ^{55}Fe, and ^{241}Pu were measured, after separation from other radionuclides, in digestion liquor or gas phase obtained from dissolution experiments performed with irradiated Zircaloy-4 using liquid scintillation counting (LSC). LSC measurements were performed using an ultra-low level spectrometer (Quantulus 1220, Wallac Oy, PerkinElmer). Up to 3 mL of sample solution were mixed with scintillation cocktail (Hionic Fluor™ or Ultima Gold™ LLT/XR, PerkinElmer) and measuring time was 3×30 minutes. Polyvials (HDPE, Zinsser Analytic) were used for liquid scintillation counting.

In addition, actinides/isotopes such as $^{235,238}U$, ^{237}Np, $^{238,239,240,241,242}Pu$, $^{241,243}Am$, and ^{244}Cm present in digestion liquors from Zircaloy-4 dissolution were also quantified using mass spectrometry. Measurements were performed using an ICP-SF-MS (inductively coupled plasma – sector field – mass spectrometer, ELEMENT XR™ ICP-MS, Thermo Scientific), which combines a dual mode secondary electron multiplier with a Faraday detector.

Samples were diluted to a volume of 5 mL using 2% HNO_3 for the measurements. Dilution ratios used in this study were 1:10, 1:100, and 1:1000 and indium was used as internal standard.

Separation techniques used in this study include extraction chromatography e.g. ^{55}Fe [2], extraction of ^{14}C by conversion into $^{14}CO_2$ and absorption in NaOH [3] as well as separation of Pu isotopes by liquid-liquid extraction [4].

INVENTORY CALCULATIONS AND SIMULATION OF A PWR GÖSGEN FUEL ASSEMBLY

The activation of the Zircaloy-4 plenum cladding, under investigation, was derived by the Monte Carlo N-particle code (MCNP 2.7), which simulates the neutron flux of the fuel assembly and the CINDER program which calculates the activation [5, 6]. By coupling of the burn-up and activation program CINDER with MCNP more accurate calculations can be performed in comparison with stand-alone activation codes such as ORIGEN [7]. The calculated flux in the activated region under investigation is introduced by 63 energy groups and thus the reaction rates are more exact in comparison to one average group used in stand-alone codes. Further, the algorithm used for the Bateman equation known as the linear chain method is considered to be

more advantageous in comparison to stand-alone codes [8]. The transport and activation cross section data are based on the ENDF/B-VII cross-section library [9].

The burn-up simulation of the subassembly was optimized into five steps. At the end of the 1226 effective full power days in the reactor, a decay period of 9600 days was considered, which corresponds to the period between the end of the irradiation in 1989 and the date of the measurements performed in this study.

The properties of the Zircaloy-4 plenum cladding such as geometrical shape, dimensions, alloying constituents and impurities, irradiation time, burn-up level, and linear power rate were accounted for in such a way, that it allows to simulate the local flux accurately.

Inventory calculation of minor actinides and fission products present in the Zircaloy-4 plenum cladding is based on 3.5 ppm natural uranium impurity found in Zircaloy-4 [10]. The inventory of the activation products is based on the respective precursor elements (e.g. ^{14}N, ^{54}Fe, ^{124}Sn) which are introduced as alloying constituent or impurity in Zircaloy-4.

Fuel rod SBS1108 was a test fuel rod and consisted of five segments containing nuclear fuel and two dummy segments to make it a full-length PWR Gösgen fuel rod. The segment N0204, where the investigated plenum was obtained from, was in the active zone of the reactor. The test fuel rod was inserted into a 15×15 PWR Gösgen fuel assembly and irradiated to the aforementioned burn-up conditions.

For the numerical simulation and in order to avoid statistical errors four equivalent fuel rods were simulated in the center of the fuel assembly (green fuel pins in figure 2). It is important to point out that the power and thus the total flux are generated in the yellow as well as in the green fuel pins shown in figure 2. However, the yellow rods are not being burned up. Consequently, the neutron flux is simulated in such a way that the characteristic output parameters e.g. average burn-up, effective full power days and average liner power rate are met.

For the 3D simulation, the axial position of the fuel rod segment and thus the plenum section under investigation, in the nuclear reactor was derived from [11-14].

The 20 positions of the guide tubes of the fuel assembly are shown as red circles in figure 2. They are filled with water of the primary cooling circuit (dark blue color). The control rods are considered fully extracted for the simulation.

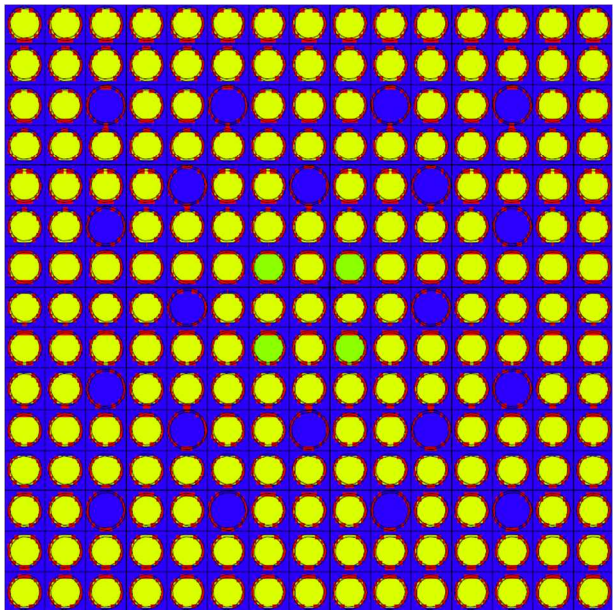

Figure 2. MCNP based graph of the simulated PWR Gösgen 15×15 fuel assembly. Consisting of 205 fuel rods (green and yellow pins) and 20 guide tubes (red circles). Water of primary cooling circuit is coloured in blue.

RESULTS AND DISCUSSION

In table 1 the experimentally determined inventories of various activation products are shown and compared to calculated inventories. A very good agreement between experimental and calculated data can be seen and the deviation between experimental and calculated (E/C) values is below 15%.

In case of minor actinides, a good agreement of E/C ratios is seen among the actinides/ isotopes series (see table 2). However, the calculated values underestimate the experimental data by a factor of about 57 ± 9. The excess inventory of minor actinides is due to fission of uranium adherences on the inner surface of the plenum not taken into account in the neutronic calculations. These uranium remnants on the inner Zircaloy surface originate from loading of fuel pellets into the cladding tube during the fuel rod fabrication process.

Table 3 shows the comparison of experimentally obtained data with calculated values for (non-)volatile fission products. In case of the non-volatile fission product ^{154}Eu the E/C ratio of 56 ± 6 is very similar to that of the minor actinides (57 ± 9). In case of the volatile fission product ^{137}Cs, the experimental data exceeds the calculation by a factor of about 114 ± 11. An E/C ratio similar to that of the minor actinides or ^{154}Eu would be expected if ^{137}Cs originates only from fission of uranium present in the plenum (U impurity in Zircaloy + U remnants on inner surface). However, the massive excess of cesium found in the plenum is due to migration of cesium released from fuel pellets during reactor operation and precipitated at the relatively cold plenum compared to the warmer fuel pellet pile.

Table 1. Comparison of experimental and calculated inventories of various activation products.

	^{14}C [Bq/g]	^{55}Fe [Bq/g]	^{125}Sb [Bq/g]
experimental	$3.7(\pm0.4)\times10^{4}$	$1.5(\pm0.1)\times10^{5}$	$2.4(\pm0.2)\times10^{5}$
calculated	3.5×10^{4}	1.3×10^{5}	2.6×10^{5}
ratio (E/C)	1.06 ± 0.11	1.15 ± 0.12	0.92 ± 0.09

Table 2: Comparison of experimental and calculated inventories of various minor actinides.

	^{239}Pu [Bq/g]	^{242}Pu [Bq/g]	^{241}Am [Bq/g]	^{243}Am [Bq/g]	^{244}Cm [Bq/g]
experimental	$1.2(\pm0.1)\times10^{4}$	$2.3(\pm0.2)\times10^{2}$	$1.7(\pm0.2)\times10^{5}$	$3.3(\pm0.3)\times10^{3}$	$3.1(\pm0.3)\times10^{5}$
calculated	2.4×10^{2}	4.1×10^{0}	3.6×10^{3}	4.9×10^{1}	4.7×10^{3}
ratio (E/C)	50 ± 5	56 ± 6	47 ± 5	67 ± 7	66 ± 7

Table 3: Comparison of experimental and calculated inventories of various fission products.

	^{154}Eu [Bq/g]	^{137}Cs [Bq/g]
experimental	$3.5(\pm0.3)\times10^{4}$	$3.3(\pm0.3)\times10^{6}$
calculated	6.3×10^{2}	2.9×10^{4}
ratio (E/C)	56 ± 6	114 ± 11

SUMMARY AND CONCLUSIONS

In general, a good agreement, between experimental and calculated inventories, is found for activation products. The experimental inventory of minor actinides as well as non-volatile fission products exceeds the calculated values by a factor of about 57 ± 9 due to nuclear fuel adhering on the inner plenum cladding surface. Three sources contribute to the massive excess of the volatile fission product ^{137}Cs in the plenum:

1. Fission of U impurity within the Zircaloy-4 (3.5 ppm).
2. Fission of nuclear fuel/U remnants deposited on the inner surface of the plenum cladding.
3. Cs volatilized from subjacent fuel pellets during reactor operation.

ACKNOWLEDGEMENTS

The authors highly appreciate the technical contribution by Melanie Böttle, Markus Fuss, Frank Geyer, Tanja Kisely, and Cornelia Walschburger of KIT.

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