The capability of the spent fuel rod to contain radionuclides during the cooling, storage and handling / transportation stages determines to a large extent the safety of nuclear fuel after discharge from the reactor. In addition to the property evolution of intact fuel rods, the behaviour of defective rods and the consequences of potential accidents causing rod failure must be considered. This paper presents the most recent results of ongoing spent fuel characterization studies focused on long-term storage and transportation performed at JRC-ITU. Irradiated fuel alterations as a function of time under the cumulative effect of alpha-decay damage and radiogenic He accumulation are investigated at the microstructural level and at the level of macroscopic properties (e.g. hardness). Properties measured on LWR fuel (UO₂, MOX) are complemented by tests on alpha-doped UO₂ which simulates ageing processes under accelerated conditions. The generic trend observed for all the measured property changes indicates that a saturation level is reached after an initial alteration stage. At very high dose, transmission electron microscopy analysis provides evidence for grain polygonization and microstructure reorganization. In addition to intact fuel rods, data on the behaviour of defective rods and the consequences of potential accidents are presented. These tests are part of a program of studies aimed at characterizing safety relevant aspects potentially affecting LWR fuel rods with different burnup, and simulating different scenarios (ages and thermal histories).

I. INTRODUCTION

Several countries are considering extended spent nuclear fuel (SNF) storage periods due to the delay in implementing disposal in a geologic repository [1]. Investigations on packages (including spent fuel and containers) stored for relatively short term did not reveal significant degradation negatively affecting the integrity of the dry storage system [2]. Since no direct measurement of stored SNF and/or packages can cover the full extension of the ageing times of interest, which is currently undefined, direct measurements must be complemented by simulations and extrapolation studies targeting specific aspects and processes which may affect properties and behaviour of SNF during many decades or centuries of storage. For instance, tests conducted under accelerated conditions are useful to verify the range of conditions that may be expected to occur in spent fuel, thus contributing to the safe implementation of storage concepts.

This paper presents an overview of the main results obtained at JRC-ITU from a programme of experimental studies investigating safety aspects of the back-end of the nuclear fuel cycle. This includes the main stages of SNF management: cooling, drying, storage, handling & transportation before and after storage, and, for the open cycle, disposal in a geologic repository. The focus is on properties and behaviour of the spent fuel rod (fuel and cladding) [3-17].

SNF is not in thermodynamic equilibrium. Alpha-decay is the main process that alters properties and behaviour of spent fuel after discharge from the reactor. The effects of alpha-decay damage in the lattice of UO₂ become evident at microstructural and macroscopic level shortly after the reactor shutdown and the end of the fission-dominated irradiation regime [3]. Possible effects of decay damage and radiogenic helium accumulation associated to long term storage are investigated [3-14]. The studies on the fuel are combined with cladding examination and characterization of eventual hydride reorientation processes. The goal of these studies is to ensure that the mechanical integrity and the functionality of all components of the containment system are retained, allowing retrievability and further handling of SNF after extended storage without the necessity of additional containment measures. The behaviour of defective SNF rods during drying, transportation and storage (or in a geologic repository) constitutes an additional area of investigation, which assumes particular relevance for nuclear power plant decommissioning schemes [14-16]. Finally, the response of the spent fuel rod to various types of mechanical loading is the object of a developing set of measurements [6, 17]. In particular, impact load tests are performed to determine the radiologic consequences of an
accident during spent fuel transportation or during severe accidents at a nuclear power plant involving fuel rod fracture and fuel dispersion. These tests are also included in the study addressing the mechanical integrity and behaviour of SNF rods after extended storage.

II. EXPERIMENTAL

"Alpha-doping" UO₂ (i.e. loading the fuel matrix with short-lived alpha-emitters) enables the study of SNF properties as a function of time under accelerated alpha-decay rate conditions. This approach can provide valuable insight on mechanisms and effects expected to occur over relatively long time interval. Sintered pellets containing ~0.1 and ~10 wt. % of ²³⁸Pu with specific alpha-activity of ~3.8·10⁹ and ~3.8·10⁸ Bq/g, respectively, were used for the measurements reported here [7, 8]. The alpha-doped compounds were prepared using sol-gel routes ensuring a homogeneous distribution of the alpha-decay events in the fuel matrix, thus avoiding anisotropy effects associated e.g. with ion beam implantation. The build-up of microstructural and macroscopic effects is measured as a function of time by a combination of techniques [3-12]: microstructure examination using Transmission Electron Microscopy (TEM), lattice parameter swelling by X-Ray Diffraction (XRD), thermal annealing by calorimetric techniques, thermal diffusivity by laserflash, thermal solubility and desorption of He by Knudsen cell with mass spectrometry, hardness by Vickers indentation. Measurements on alpha-doped UO₂ are compared with similar analyses on irradiated fuel as much as possible.

Capped commercial PWR spent fuel rod segments with an average burn-up of 56 GWd/t containing pre-set defects were tested at 90°C in autoclave in presence of water. Three gas atmospheres were used in the autoclave: I argon (3.4 bar); II a mixture of argon and hydrogen (2.9 bar, ~93 vol.% H₂); III pure hydrogen (3.8 bar). The experiments lasted for ~5 months (Ar, Ar/H₂) and ~3 months (H₂). The stainless steel autoclave and a remotely driven oven were adapted for remote handling inside a concrete hot cell (Fig.1 (a)). The autoclave was equipped with temperature and pressure sensors. Attached gas lines allowed preliminary purging and initial pressurising of the autoclave. Gas samples were collected from the autoclave by using a special gas-mouse adapter. The autoclave had an inner volume V₁ of 185.5 cm³. The volume of the gas tubes V₂ connected to the autoclave volume was ~7 cm³. The total gas volume was V₉0= 142 cm³, with 30 cm³ water at the bottom of the autoclave. The temperature in the gas tubes was not controlled, which resulted in water condensation on the colder wall inner sections. Directly above the autoclave lid 60°C – 70°C were measured.

The SNF sample was placed on a stainless steel stand (Fig. 1(b)) inside the autoclave to avoid direct contact between the capped fuel rodlet and the water at the bottom of the autoclave. An essentially constant burn-up of ~59 GWd/t was calculated for the rodlets.

Three parallel cuts (0.5 mm wide) through the cladding were made in the uncovered area to simulate defects.

After the test, defect surface areas of the rodlets were examined by Scanning Electron Microscopy (SEM). Furthermore, the composition of the gaseous and water phase were analysed by mass spectrometry. Half of the sampled liquid was acidified in 1 M HNO₃. Blanks were prepared in order to check for possible contaminations coming from the hot cell environment during the sampling procedure. After removing the water, the autoclave was rinsed with 1 M HNO₃ for 3h at 60°C, and subsequently with deionised water at 90°C for 2.5 days and 1 day to collect material precipitated on the inner walls during the corrosion test:

The fracture behaviour and fuel dispersion out of LWR spent fuel rod segments subjected to simulated impact loading has been characterized in the frame of a collaboration and with the support of GNS (Germany) and AREVA [17]. In this set of tests a falling hammer device was used to impact on UO₂ fuel rodlets at ambient temperature and pressure. The rodlets were from PWR and BWR with burnup ranging between 19 and ~74 GWd/THM.
III. EFFECTS OF ALPHA-DECAY DAMAGE AND HELIUM ACCUMULATION ON UO₂ PROPERTIES

If we assume a storage duration of up to ~100 y, the damage level induced by alpha-decay is of the order of 0.2 – 0.4 dpa (displacement per atom) for UO₂ fuel up to 60 GWd/t, and is >1 dpa in the case of MOX. The calculated helium generation for UO₂ SNF would be in the range 10⁶ – 10⁷ g per g of fuel, depending on the burnup [13]. This would correspond to a maximum He concentration of ~0.1 at% or ~0.25 cm⁻³ per cm³ of fuel.

The typical trend of the properties measured as a function of accumulating alpha-decay damage in alpha-doped UO₂ (accelerated conditions) shows a saturation of the property change. Thermal properties (diffusivity, heat) and hardness reach saturation at 0.1-0.2 dpa, corresponding to a storage time of several decades (< 100 y). This behaviour is associated to the formation of microstructural defects due to radiation damage. In particular, TEM analysis of alpha-doped UO₂ and irradiated fuel allows characterizing the formation of dislocation loops already at very low dose [11-12] (point defects being not detectable by microscopy). A somewhat different trend is shown by the fractional increase of the lattice parameter, which shows saturation at a swelling of 0.4-0.5%, corresponding to ~1.2 dpa. Such level of damage would require storage times of several centuries for UO₂, but could be reached within 100 y in the case of spent MOX fuel [13]. The maximum increase of the lattice parameter (~0.5%) is higher than some reported values at saturation for UO₂ and other actinide oxides [18-22]. Eyal [20] reviewed the reported saturation levels of the lattice parameter increase caused by alpha-decay for different actinide oxides: the values generally fell within the interval between ~0.23 % and ~0.35 %. The additional swelling observed at higher dose in the present case is probably associated to the accumulation of He. The thermal desorption measurements indicate that essentially all the helium produced by alpha-decay in alpha-doped UO₂ is retained in the solid up to ~3 dpa [4, 11-12]. The analysis of He incorporation in the UO₂ lattice and lattice swelling was addressed also by ab initio calculations [23-24] and by experimental and modelling studies [5, 7, 11, 25-27]. TEM analysis reveals the formation of nano-sized helium bubbles at damage levels near 0.4-0.5 dpa [11-13].

The assessment of the applicability of these results to the case of spent fuel during extended storage is still ongoing. For some properties, the trends observed under accelerated conditions have been validated by spent fuel analyses. For instance, the basic effects of alpha-decay damage accumulation on the microstructure [13] and on the thermal transport properties [3] are the same. The discrete thermal recovery steps of the radiation damage and the corresponding temperatures are also the same [3]. The helium thermal release behaviour appears very similar [13]. The trends observed in the hardness measurements of alpha-doped samples are currently being validated with tests performed on irradiated fuel with different burnup levels after different storage periods. Unequivocal validation of the lattice swelling behaviour observed in alpha-doped UO₂ for the case of irradiated fuel is not yet available.

Up to a damage level > 3 dpa none of the alpha-doped UO₂ samples used for the present multi-year investigation has shown significant loss of mechanical integrity. This is in agreement with the results by Ferry et al. [25] who estimated the critical amount of helium necessary to cause fuel cracking.

IV. DEFECTIVE SPENT FUEL RODLET TESTING IN AUTOCLAVE

The maximum gas pressure increases in the autoclave for experiments I, II and III were 11%, 7% and 6%, respectively. In experiment I the main species evolved in the gas phase was Xe, followed by radiolytically produced H₂ (corresponding to half and one third of the gas pressure increase, respectively). He, CO₂, N₂, H₂O and Kr were found in the 10⁻³ range; O₂ was below the detection limit. The relative compositions of the other final gases are very similar. The main compounds are the fission gases Xe, Kr and the radiogenic He. In H₂/Ar the O₂ level was below 5 ppm (detection limit). In the last experiment under H₂ an O₂ concentration in the range of 10 – 20 ppm was detected. The latter may result from a possible in leakage during the gas-MS measurement.

An overview of the solution analysis results for experiment II (H₂/Ar atmosphere) is given in Table 1 (a) and (b). It has to be noted that the surface, which has contributed to the release is in fact much larger than the geometrical area of the pre-set cuts (~0.67 cm²), but not quantifiable due to the cracking pattern and the uncertainties in defining the real surface area exposed to water contact. Due to the high humidity conditions in the autoclave, a thin water film covered the fuel rodlet. This water film allowed the transport of released nuclides into the water reservoir at the bottom of the autoclave. ICP-MS analysis of water samples after the test confirmed that significant dissolution occurred for the mobile fission products Cs and I. γ-spectrometry measurements were used to evaluate the Cs contents in experiments I and II. In general the ICP-MS results for ¹³⁷Cs were in good agreement with the γ-spectrometric ones. The release of Cs was for the three experiments in the range of 6.9 mg – 7.7 mg. Iodine values were ~0.6 mg (Ar) and ~0.9 mg in the case of H₂. For H₂/Ar the measured value was much lower (~0.09 mg); it is assumed that I was somehow lost during solution sample preparation. Other fission products were detected, but their concentration was orders of magnitude lower. In the case of redox-sensitive
technetium, the release decreased significantly moving from Ar to H$_2$/Ar and to pure H$_2$. Mo showed a slight decrease in solution from experiment I to III (Ar to H$_2$).

The determination of U and Pu was affected by uncertainties due to the presence of fines and other technical issues. U and Pu were found in the concentration range $10^{-8}$ - $10^{-7}$ mol/l and $10^{-10}$ - $10^{-9}$ mol/l, respectively. No clear overall trend could be identified for these actinides.

Table 1(a): water and rinse solution analysis results of experiment II (H$_2$/Ar atmosphere; 143 days). Values in bold refer to solution analysis; values in bracket are deemed not fully reliable (due to low content or other measurement issues).

<table>
<thead>
<tr>
<th>conc. mol/l</th>
<th>Rb (fiss)</th>
<th>Mo (fiss)</th>
<th>$^{99}$Tc</th>
<th>$^{127+129}$I*</th>
</tr>
</thead>
<tbody>
<tr>
<td>solution</td>
<td>3.0E-5</td>
<td>2.1E-6</td>
<td>1.5E-9</td>
<td>3.9E-5</td>
</tr>
<tr>
<td>acidified</td>
<td>1.8E-5</td>
<td>1.3E-6</td>
<td>1.1E-9</td>
<td>1.6E-6</td>
</tr>
<tr>
<td>rinse 1</td>
<td>8.2E-7</td>
<td>(6E-8)</td>
<td>(2E-9)</td>
<td>2.6E-7</td>
</tr>
<tr>
<td>rinse 2</td>
<td></td>
<td></td>
<td>(2E-9)</td>
<td>5.1E-7</td>
</tr>
<tr>
<td>rinse 4</td>
<td></td>
<td></td>
<td>(3E-10)</td>
<td>1.3E-7</td>
</tr>
<tr>
<td>mass loss mg</td>
<td>4.3E-2</td>
<td>3.4E-3</td>
<td>2.8E-6</td>
<td>(8.8E-2)</td>
</tr>
<tr>
<td>rinse 1+2</td>
<td>3.4E-3</td>
<td>(3E-4)</td>
<td>(2E-5)</td>
<td>(5.1E-3)</td>
</tr>
<tr>
<td>mass loss mg/m$^2$</td>
<td>637</td>
<td>51</td>
<td>0.04</td>
<td>(1319)</td>
</tr>
</tbody>
</table>

$^{*}$I concentration measurements 9 weeks after sampling.

Table 1(b): water and rinse solution analysis results of experiment II (H$_2$/Ar atmosphere; 143 days). Values in bold refer to solution analysis; values in bracket are deemed not fully reliable (due to low content or other measurement issues).

<table>
<thead>
<tr>
<th>conc. mol/l</th>
<th>Cs(Ba)$^*$ (fiss)</th>
<th>$^{133}$Cs</th>
<th>$^{139}$La</th>
</tr>
</thead>
<tbody>
<tr>
<td>solution</td>
<td>2.7E-3</td>
<td>1.1E-3</td>
<td>1.4E-7</td>
</tr>
<tr>
<td>acidified</td>
<td>1.8E-3</td>
<td>7.2E-4</td>
<td>9.1E-8</td>
</tr>
<tr>
<td>rinse 1</td>
<td>9.2E-5</td>
<td>3.2E-5</td>
<td>1.3E-8</td>
</tr>
<tr>
<td>rinse 2</td>
<td>7.3E-6</td>
<td>2.8E-6</td>
<td>(2E-9)</td>
</tr>
<tr>
<td>rinse 4</td>
<td>1.9E-7</td>
<td>1.6E-7</td>
<td>1.5E-9</td>
</tr>
<tr>
<td>mass loss mg</td>
<td>6.2</td>
<td>2.5</td>
<td>3.3E-4</td>
</tr>
<tr>
<td>rinse 1+2</td>
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<td>0.23</td>
<td>1.1E-4</td>
</tr>
<tr>
<td>mass loss mg/m$^2$</td>
<td>9.3E4</td>
<td>3.8E4</td>
<td>5</td>
</tr>
</tbody>
</table>

$^{*}$sum of $^{133}$Cs, $^{135}$Cs ($^{134}$Ba), $^{137}$Cs ($^{135}$Ba), $^{131}$Cs ($^{137}$Ba).

Samples for SEM-EDS analysis were prepared adopting a special cutting technique to ensure that the corroded fuel surfaces remained unaffected by the preparation. SEM examination of the rodlet exposed for 150 days to humid Ar-atmosphere at 90°C showed a slightly altered surface and grain boundary attack in the area of the defect. On both rodlets exposed to the moist hydrogen-containing atmosphere (experiments II and III), no visible fuel surface alteration could be detected. EDS analysis of the hydrogen-exposed surfaces showed, in addition to uranium, only the presence of fission products caesium and barium at the outer periphery of the fuel pellet, near the fuel cladding. Here also zirconium traces were found. Other elements were below the detection limit of the device. The fuel exposed to pure Ar could not be examined by EDS due to the high radioactivity of the samples producing an excessive background level.

V. IMPACT LOAD TESTS

Figure 2 shows two photographs recorded by a high speed camera placed outside the hot cell showing the fracturing of the ~74 GWd/THM PWR rodlet. Remarkable similarities were observed among all rodlets tested; in particular, the amount of fuel released per fracturing is comparable to that released from the other samples. In all the tests the released fuel collected at the bottom of the device corresponded to < 2g per fracture (aerosol and fine particulate fractions were not measured during these tests). Impact test results on irradiated fuel rods/elements were reported by Purcell and Dallongeville [28]. The tests were performed on high burn-up LWR fuel rods applying bending loads to pressurised rod specimens previously subject to axial impact. The authors indicated that the fuel release was < 10 g per break. Given the different modes of testing, the results are in good agreement with the present ones.
Figure 2 (a) and (b). High speed camera photograms illustrating the impact fracture of a ~74 GWd/tHM PWR fuel rodlet from [17].

The images in Figure 3 clearly show that no fuel "flow-out" behaviour occurred, and no special fuel release effects associated with the presence of the rim structure were observed for the high burnup samples. The results indicate that only the fuel volume directly affected by the fracture of the rodlet was released.

Figure 3 (a) and (b). Corresponding fracture surfaces of a PWR fuel rodlet with 43 GWd/tHM after the impact test.

VI. SUMMARY AND CONCLUSIONS

A research programme at JRC-ITU is devoted to the investigation of spent fuel safety aspects, including handling, transportation, extended storage and retrievability after storage. Intact and defective fuel rods are considered under normal conditions and accident scenarios.

An effective assessment of the behaviour of used fuel during and after storage requires simulation and extrapolations as a complement for direct analysis of irradiated fuel, since measurements on SNF rods with the required age are not possible today. The effects due to the accumulation of alpha-decay damage and helium are studied using accelerated conditions using alpha-doped materials.

The evolution of most properties as a function of accumulated radiation damage follows a typical saturation trend. Thermal properties and hardness saturate at 0.1-0.2 dpa, corresponding to a few decades of SNF storage; this is probably associated with the formation of dislocation loops and point defects in the lattice. Lattice swelling in alpha-doped UO₂ saturates at ~1.2 dpa, corresponding to several centuries of storage. The maximum swelling observed is higher than values typically associated with radiation damage in actinide oxides; this is probably due to helium retention in the solid up to relatively high dose and formation of small He bubbles. While microstructure and thermal property trends (including He desorption) observed in alpha-doped UO₂ have been validated for spent fuel, the applicability of the swelling trend has still to be assessed. The application of these findings to spent fuel requires factoring in specific characteristics of irradiated fuel linked to its heterogeneity.
Limited surface alteration and grain boundary etching was observed after up to 4 months of testing defective SNF rods in autoclave in humid environment under inert atmosphere; less alteration was observed in presence of hydrogen. Pressure build-up including radiolytic hydrogen production and fission gas release was measured. Solution analysis revealed high concentrations of the mobile fission products Cs and I dissolved in water due to condensation films contacting the fuel.

Impact load testing of LWR spent fuel rodlets at ambient temperature and pressure revealed no special fuel release effects associated with the presence of the rim structure for high burnup samples. Moreover, no "flow-out" of fuel pellets associated with the presence of an open gap between fuel pellet and cladding was observed in the case of low burnup fuel.

The programme of measurements will be extended to cover higher dpa levels and other thermal and mechanical conditions experienced by SNF rods in order to gain full understanding of the mechanisms affecting very long-term spent fuel storage and retrievability thereafter. High dpa studies are also relevant for the prediction of the long-term evolution of spent fuel in a geologic repository.

The ultimate goal of this campaign is to obtain a unified picture of the low temperature evolution of spent fuel and cladding properties under the effect of accumulating radiation (decay) damage and helium generation.

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