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Modern Spent Fuel Dissolution and
Chemistry in Failed Container Conditions

DISCO

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DELIVERABLE D3.1

Spent fuel experiments: First dissolution results

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1 Introduction

The EURATOM DisCo (*Modern spent nuclear fuel Dissolution in failed container Conditions*) focuses on the dissolution of nuclear fuel which contain additives (such as Al and Cr) as well as the dissolution of mixed-oxide fuel containing a certain amount of Pu (MOX fuel). Besides dissolution studies with doped UO_x fuels and MOX fuels, numerical models are going to be developed to enhance our understanding of these modern fuels in comparison with traditional nuclear fuels, so-called “standard UO_x fuels”.

This report summarizes the progress made in Work Package 3 of DisCo between the ninth month of the project and the end of the second year of the project. The main goal of WP3 is to study experimentally the matrix dissolution of spent UO_x fuels containing dopants as well as MOX fuels under relevant disposal conditions. The research groups that contributed with experiments on dissolution of such irradiated UO_x and MOX fuels within WP3 are Fundacio CTM Centre Tecnologic – now Fundacio Eurecat (EURECAT) in conjunction with Universitat Politècnica de Catalunya (UPC), Joint Research Centre (JRC-KA), Karlsuher Institut für Technologie (KIT-INE) and Studsvik Nuclear AB (STUDSVIK). The release of radionuclides from the matrix of each spent nuclear fuel (SNF) as well as the instant release fraction of these fuels are determined by the four research groups in dissolution experiments in laboratories in Karlsruhe (JRC-KA and KIT-INE) and Nyköping (STUDSVIK), which are equipped with “hot” installations such as a shielded glove box, a shielded box line or hot cells.

Current experiments are performed and future experiments will be performed with two BWR UO_x fuels having a burnup of 57 and 59 $MWd\cdot(kg_{HM})^{-1}$, with two PWR MOX fuels of 38 and 54 $MWd\cdot(kg_{HM})^{-1}$ as well as two PWR UO_x fuels of 58 and 73 $MWd\cdot(kg_{HM})^{-1}$ (average burnups). Table 1-1 presents characteristic fuel data, sample types, solution types and gas atmospheres of the dissolution experiments. Details on the two BWR UO_x fuels are given by Metz et al. [1,2] and details on the PWR MOX fuel with of 38, 54 and 58 $MWd\cdot(kg_{HM})^{-1}$ are given by Farnan et al. [3].

The first 15 months of WP3 (i.e. project month 9 to 24) have been used to define the detailed experimental matrix and to prepare the dissolution experiments and analytical methods. The sample preparation methods, leachant composition and analytical methods have been discussed between the participating institutes, to come to an optimal program in which the various contributions give complementary information, produced in conditions that are sufficiently harmonized to allow intercomparison.

At the laboratories in Karlsruhe and Nyköping, fuel rods had been cut into segments and two general types of fuel samples had been prepared: (a) fuel segments with their Zircaloy claddings, denoted as “cladded segments”; (b) fragments of the fuel matrix without any cladding material, denoted as “fragments”. Samples of the two BWR UO_x fuels and the PWR UO_x fuel of 73 $MWd\cdot(kg_{HM})^{-1}$ burnup had been prepared already before the onset of DisCo. Preparation of cladded segments and fragments from PWR MOX fuel with of 38, 54 and 58

MWd·(kg $_{HM}$)$^{-1}$ were performed in the framework of Work Package 2 of H2020-project DisCo (Farnan et al. [3]).

Table 1-1: Characteristic fuel data, sample types, solution types and gas atmospheres of dissolution experiments with spent UO$_x$ fuels and spent MOX fuels.

sample name	**fuel type**	**reactor type**	**average burn-up [GWd/t]**	**sample type**	**solution**	**gas atmosphere**
5A2	standard UOx	BWR	57	fragments	NaCl-BIC	H2 55 bars
C1	Al-Cr-doped UOx	BWR	59	fragments	NaCl-BIC	H2 55 bars
KWU11.38-5810	MOX	PWR	38	fragments	NaCl-BIC	H2 3 bars
KWU11.38-5810	MOX	PWR	38	cladded segment	NaCl-BIC	H2 3 bars
73BIC	standard UOx	PWR	73	cladded segment	NaCl-BIC	air
73YCWCa	standard UOx	PWR	73	cladded segment	YCWCa	air
/experiment to be started/	MOX	PWR	54	cladded segment	NaCl-BIC	H2 >20 bars
/experiment to be started/	Cr-doped UOx	PWR	58	fragments	NaCl-BIC	H2 >20 bars
/experiment to be started/	standard UOx	PWR	73	cladded segment	NaCl-BIC	Ar
/experiment to be started/	standard UOx	PWR	73	cladded segment	YCWCa	Ar

Diluted NaCl solution with 1 to 2 mM $NaHCO_3$ (pH ~ 8, denoted as NaCl-BIC) and so-called “Young Cement Water with Calcium”, a diluted solution NaOH, $Ca(OH)_2$ solution, containing 77 mM Na_2CO_3 and other minor constituents (pH ~ 13.5, denoted as YCWCa) are used in the dissolution experiments as leachants (Table 1-1). Most dissolution experiments are conducted under hydrogen or argon/hydogen overpressure with a H_2 partial pressure between 3 and 50 bars. Additionally, two experiments with PWR UO$_x$ fuel of 73 MWd·(kg $_{HM}$)$^{-1}$ burnup are conducted in air; similar experiments with the same type of spent nuclear fuel will be conducted under Ar atmosphere (Table 1-1).

In the following sections initial results of the dissolution experiments with irradiated UO$_x$ and MOX fuels performed by KIT-INE and STUDSVIK and strongly reducing conditions, as well as by EURECAT dissolution experiments with an irradiated UO$_x$ fuel under oxic conditions are presented. Since there were delays in the documentation, with the sample preparation of the fuel samples and the autoclaves to be used in the anoxic dissolution experiments of JRC-KA and EURECAT, start of some of their experiments is expected in the third year of the project.

2 Initial results of dissolution experiments with irradiated PWR MOX fuel (73 $MWd/kg_{(HM)}$) performed by KIT

Within WP3 of DisCo, studies by KIT-INE provide experimental data concerning the matrix dissolution of an irradiated PWR MOX fuel (73 $MWd \cdot (kg_{HM})^{-1}$) under reducing conditions. Besides radionuclide release from the fuel matrix, the instant release fraction of safety relevant radionuclides are determined in these dissolution experiments, too. For this purpose, two experiments with (a) a cladded segment and (b) fragments of the spent nuclear fuel (SNF) are currently conducted in the shielded box-line of KIT-INE with periodical sampling campaigns of the gaseous and the aqueous phase. In the following, the experimental conditions and initial results of radionuclides released into the aqueous phase up to 160 days of leaching are presented.

2.1 Details of dissolution experiments with irradiated PWR MOX fuel at KIT

The dissolution experiments are performed in stainless steel autoclaves with Ti-liners under Ar/H_2 atmosphere. The starting date of each experiment is given in the following:

- Experiment with a cladded segment started on May 16, 2018.
- Experiment with fragments started on May 23, 2018.

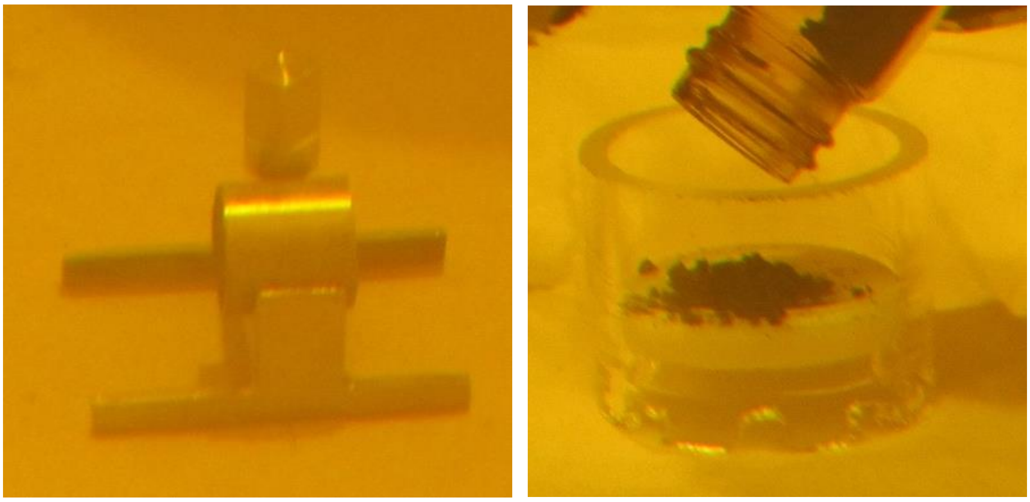
As leachant bicarbonate water (NaCl-BIC type), containing 19 mM NaCl and 1 mM $NaHCO_3$ is used. The leachant was prepared in a glove box under Ar atmosphere, with ultrapure water purified with a Milli-Q academic apparatus (Millipore, 18.2 MΩcm, 22 ± 2°C, pore size 0.22 µm) and analytical grade chemicals (Merck GmbH).

After preparation and analysis of the leaching solution, the SNF corrosion experiments were started. As a first step, the cladded segment was mounted in a titanium sample holder to ensure the contact of both pellet surfaces with the solution, and the fragments were placed in a quartz glass basket, see Figure 2-1.

In a second step, once each of the SNF samples was placed inside its respective autoclave, the lid was closed and the autoclave was flushed with Ar, to remove residual air out of the autoclave and to avoid air intrusion. Afterwards, each autoclave was filled with (230 ± 5) mL of the leachant. Finally, the total gas pressure was adjusted to 40 bar using an Ar/H_2 gas mixture (with volume fractions of 92% of Ar and 8% of H_2; provided by Basi and Schöberl GmbH) to create strongly reducing conditions (H_2 partial pressure: 3.2 bar).

After one day of exposure, the first gaseous and liquid samples were taken and analysed. After this so-called washing step, the solution was completely exchanged, in order to reduce the amount of caesium in solution and a possibly present pre-oxidised layer on the sample surfaces. A volume of (230 ± 5) mL of fresh bicarbonate solution was used for replenishment, and the Ar/H_2 atmosphere was again restored, following the procedure previously described.

Figure 2-1: Spent PWR MOX fuel samples used for two dissolution experiments under argon / hydrogen atmosphere at KIT-INE. Cladded segment fixed on sample holder and placed on bottom of an autoclave (left image); placing of fuel fragments in quartz glass basket, which was placed on bottom of autoclave before onset of the second dissolution experiment (right image).



Throughout the leaching experiments, sampling campaigns of the gaseous phase (with a sampling aliquot of (50.0 ± 2.5) mL volume) and liquid phase (with a sampling aliquot of (10 ± 1) mL volume) are performed periodically. During each liquid sampling, the headspace of each autoclave is purged with Ar, and afterwards the initial pressure conditions described above were restored using the Ar/H_2 gas mixture. Except for the first sampling (i.e. so-called washing step), the solution is not replenished after the samplings.

2.2 Analytical methods applied in SNF dissolution studies at KIT

Concentrations of actinides and technetium in aqueous solutions were determined using high-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS) A sector field device (ELEMENT XR, ThermoFisher Scientific) was used to quantify ^{99}Tc, ^{235,238}U, ^{237}Np, ^{239,240,242}Pu, ^{241,243}Am, and ^{244}Cm.

Liquid scintillation counting (LSC, Quantulus 1220, Wallac Oy, PerkinElmer) was used to quantify aqueous concentration of ^{90}Sr. Firstly, ^{90}Sr was extracted from the liquid sample aliquots by chromatography using a Sr-Resin crown ether (4,4’(5’)-di-t-butylcyclohexano-18-crown-6). Then, solution aliquots were homogenized in Polyvials (HDPE, Zinsser Analytic) with LSC-Cocktail (Ultima Gold LLT, Perkin Elmer) for the measurements.

Aqueous concentrations of ^{134}Cs and ^{137}Cs were quantified using γ-spectroscopy. Measurements 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 done 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.). APEX screw-cap microcentrifuge tubes (2 mL, polypropylene, Alpha Laboratories Ltd.) were used as sample vessels during the measurements.

2.3 Results and discussion of studies with irradiated PWR MOX fuel at KIT

Aqueous concentrations of fission products ^{90}Sr, ^{99}Tc, ^{129}I and ^{137}Cs as a function of leaching time are shown in Figure 2-2. After about 160 days of leaching, concentrations of ^{90}Sr and ^{137}Cs are still increasing. In the first two samplings, aqueous concentrations of ^{99}Tc and ^{129}I were below detection limit. Aqueous concentrations of the volatile fission products ^{129}I and ^{137}Cs are similar, and those of the matrix bound fission products ^{90}Sr and ^{99}Tc are similar, respectively.

Aqueous concentrations of the studied actinides are shown as a function of leaching time in Figure 2-3. Uranium concentrations increase in both experiments to about 10^{-7} M whereas the concentration of ^{237}Np decreases over time to below 10^{-10} M. Concentrations of other actinides in both experiments seem to be virtually constant since the first day of leaching.

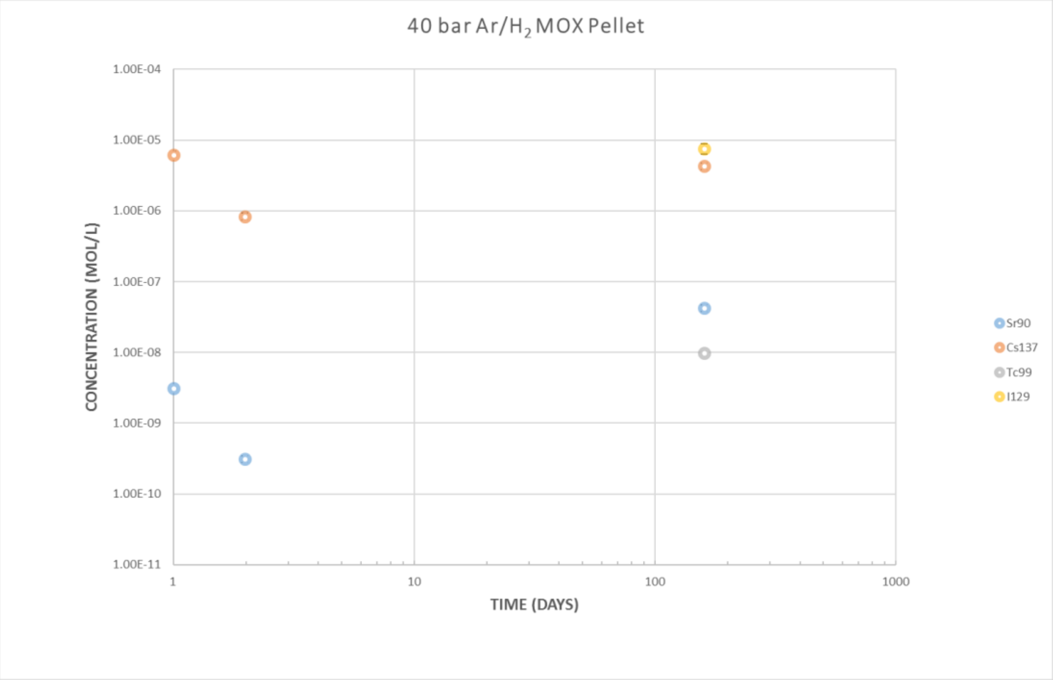
The fraction of the radionuclide inventory released into the aqueous phase is calculated to compare the release behaviour of the different radionuclides and to assess the corrosion of the spent MOX fuel. The fraction of inventory of a radionuclide *i* released in the aqueous phase, $FIAP_i$, is given by equation 1.

$$FIAP_i = \frac{m_{i,aq}}{m_{i,SNF}} = \frac{C_{(i,n)} \cdot V_{aq}}{m_{SNF} \cdot H_i} \tag{1}$$

where $m_{i,aq}$ is the mass of radionuclide *i* in the aqueous phase (g), $m_{i,SNF}$ the mass of radionuclide *i* in the spent nuclear fuel sample (g), m_{SNF} is the mass of SNF sample used in the experiment (g), H_i corresponds to the fraction of inventory for the radionuclide *i* (g/g), C_i is the concentration of element *i* in solution (g·mL^{-1}) and V_{aq} is the volume of solution (mL).

FIAP data is shown in Figure 2-4 and Figure 2-5 for fission products and actinides, respectively. Qualitatively, the temporal evolution of FIAP values of the studied fission products and actinides are similar to the evolution of the aqueous concentrations of the respective radionuclides. Quantitatively, it is obvious from the FIAP data that ^{129}I and ^{137}Cs release is significantly incongruent, i.e. two to four orders of magnitude higher than FIAP values of ^{90}Sr and ^{99}Tc, uranium and actinides. The considerable ^{129}I and ^{137}Cs release is related to a fast dissolving ^{129}I and ^{137}Cs fraction in the SNF samples. In contrast to other UO_2 matrix bound elements, ^{90}Sr is continuously released.

Figure 2-2: Aqueous concentrations of ^{90}Sr, ^{99}Tc, ^{129}I and ^{137}Cs as a function of leaching time in experiments performed with cladded MOX pellet (upper diagram) and MOX fragments (lower diagram) under hydrogen overpressure.



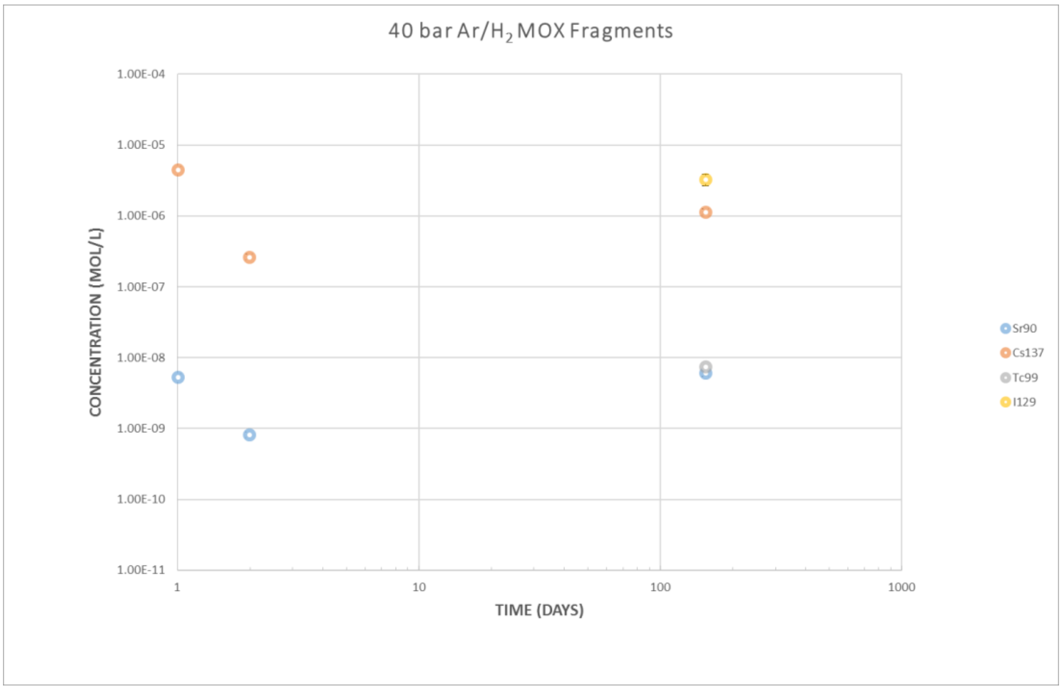
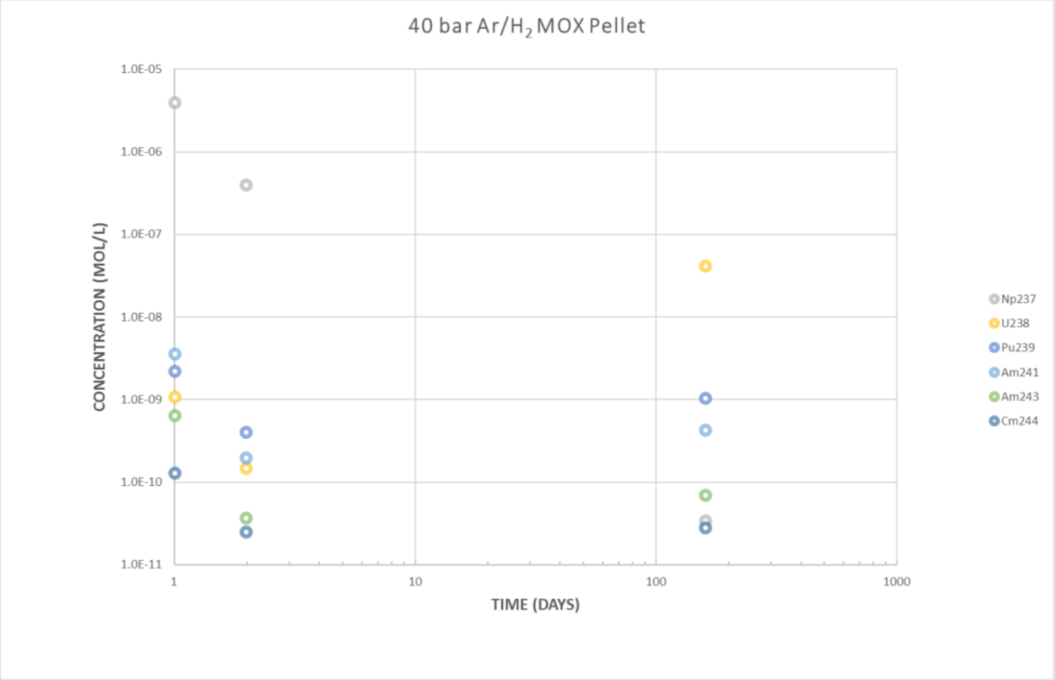


Figure 2-3: Aqueous concentrations of studied actinides as a function of leaching time experiments performed with cladded MOX pellet (upper diagram) and MOX fragments (lower diagram) under hydrogen overpressure.



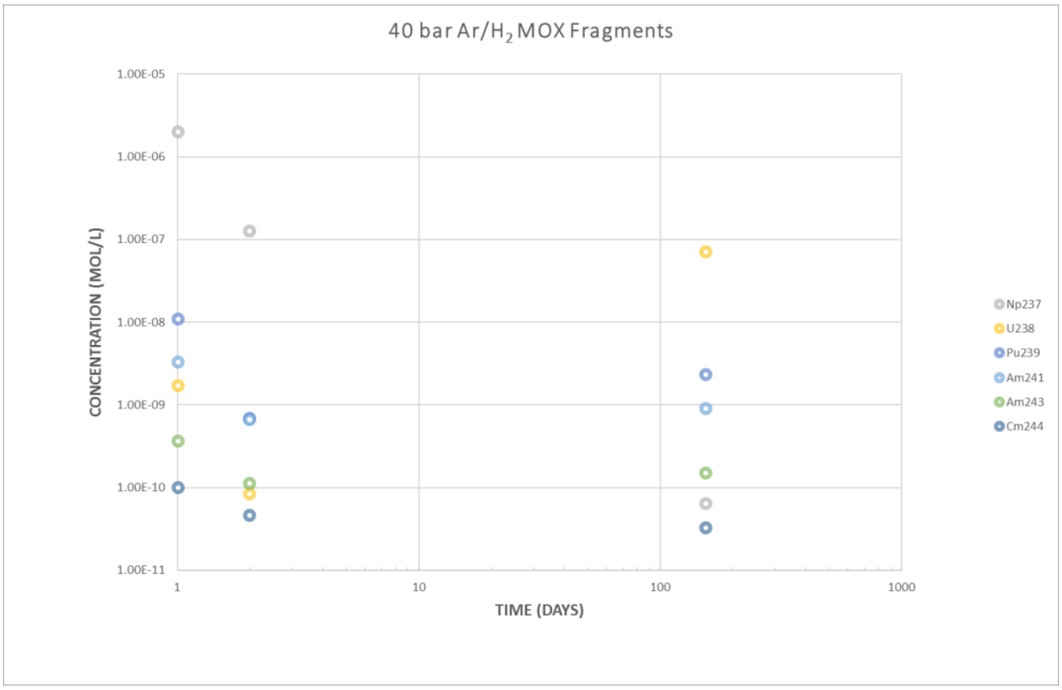
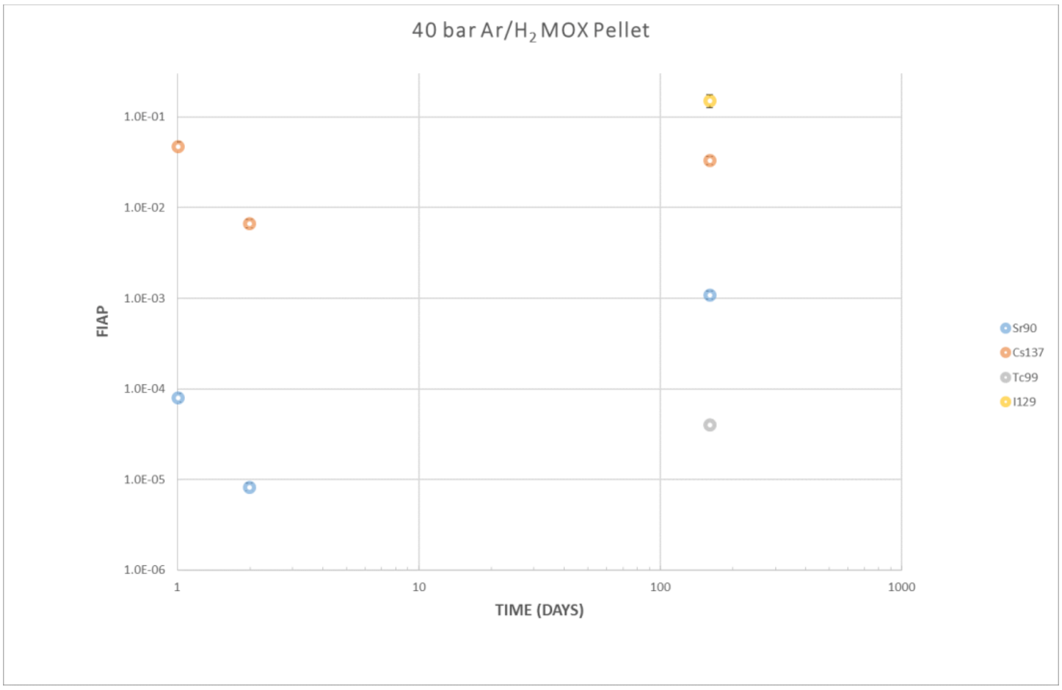


Figure 2-4: FIAP of ^{90}Sr, ^{99}Tc, ^{129}I and ^{137}Cs as a function of leaching time in experiments performed with a pellet (upper diagram) and fragments (lower diagram).



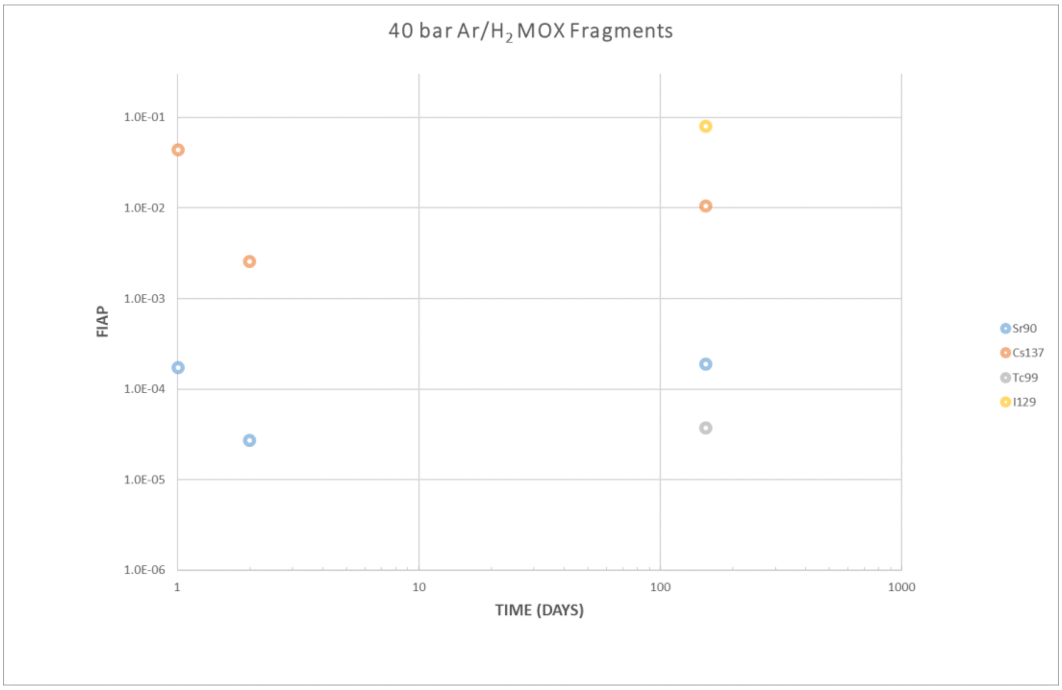
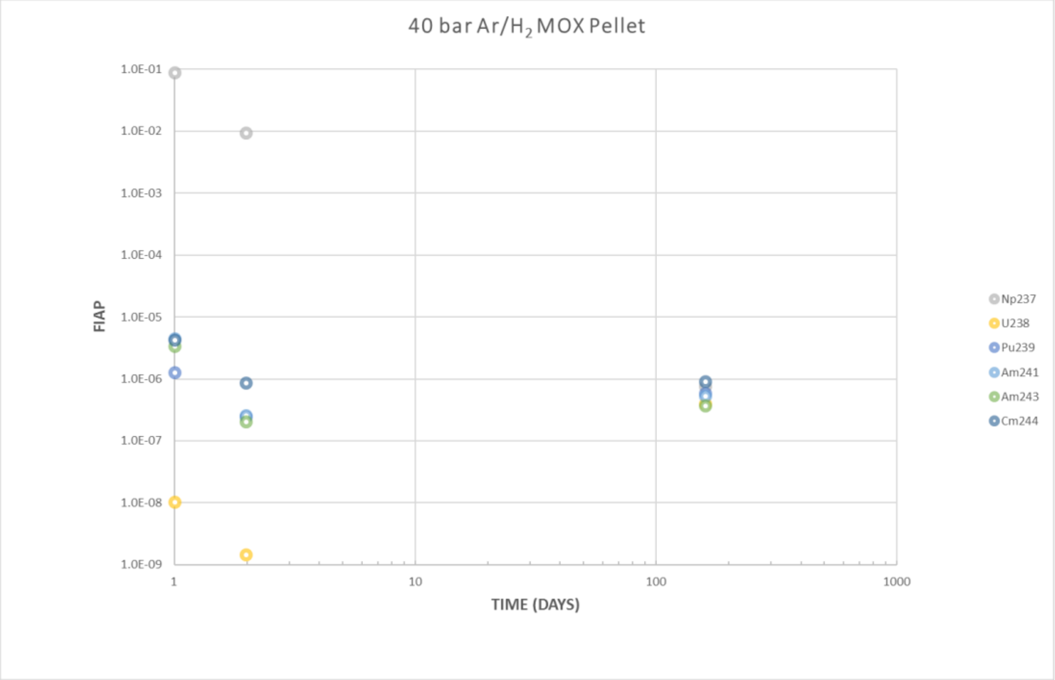
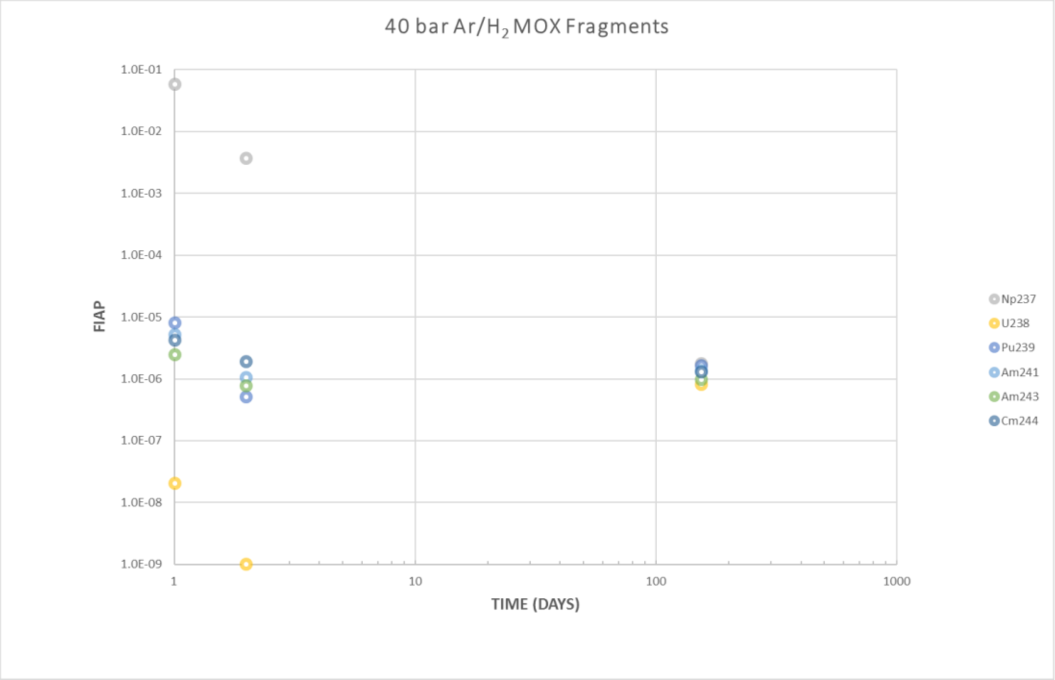


Figure 2-5: FIAP of various actinides as a function of leaching time in experiments performed with a pellet (upper diagram) and fragments (lower diagram).





3 Initial results of dissolution experiments with irradiated BWR UO_x fuels (57 and 59 $MWd/kg_{(HM)}$) performed by STUDSVIK

Studsvik is contributing to WP3 of DisCo with two dissolution experiments on a standard UO_x fuel and a Al-Cr-doped UO_x fuel, both irradiated in a BWR and achieving a similar average burnup. Improving reactor performance and reliability, reducing fuel cycle cost and the consequences of fuel failure are constant challenges for the nuclear industry. For this reason, in recent years new types of fuel have been developed. One example is the ADOPT fuel (Advanced Doped Pellet Technology) which consists of a UO_2-based fuel doped with small amounts of Cr_2O_3 and Al_2O_3. One of the main characteristics of this fuel is the enlarged grain size which results in lower Fission Gas Release (FGR) and increased density [4].

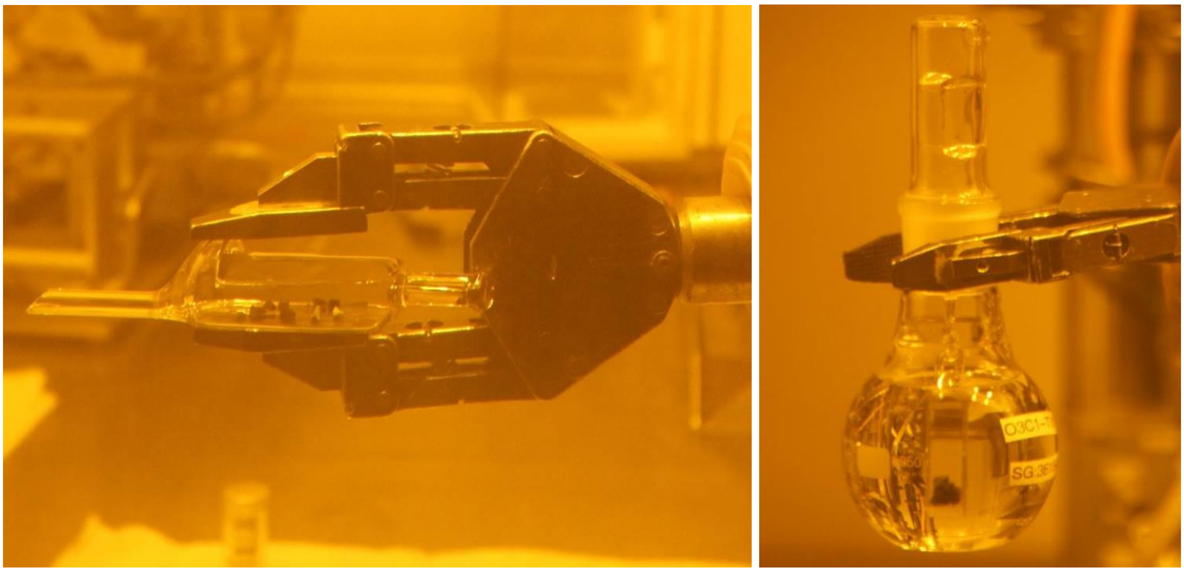
From the safety perspective of a deep geological repository for SNF, the new type of fuels must fulfill the acceptance criteria of low solubility under relevant repository conditions. Minor modifications on the UO_2 matrix resulting in property changes might affect the leaching behaviour of the fuel. For this reason, it is important to gather new data on the dissolution behaviour of a new type of fuel with additives under reducing conditions in presence of hydrogen. In the dissolution experiments of STUDSVIK, the behaviour of the doped fuel (ADOPT) will be compared to the performance of standard UO_2 fuel under identical conditions. The objective of this study is to gather data that will be used to support or refute the hypothesis that there is no significant difference in leaching behaviour between the two fuels. In addition, thermodynamic and kinetic models will be developed in WP5 of DisCo using the experimental data.

3.1 Experimental and analytical details of dissolution studies with irradiated BWR UOx fuels at STUDSVIK

The experiments are being performed on fuel fragments without cladding. The selected fragments are the same samples leached in a previous EURATOM project, FIRST-Nuclides, which were used to establish the instant release fraction and the matrix dissolution behaviour under aerated conditions [1,5]. Characteristic data of the studied SNF samples "5A2" (standard UO_x fuel) and "C1" (ADOPT, Al-Cr-doped UO_x fuel) are given in Table 1-1. The two fuels have very similar power histories, having been irradiated in the same assembly. In puncturing tests, a fission gas release of 2.4% was determined for 5A2 and 1.4% for C1, respectively.

The fuel fragments (2 g from each fuel type) were exposed to an initial leaching period (pre-wash) under aerated conditions in 200 ml 10:10 mM $NaCl:NaHCO_3$ solutions (NaCl-BIC type) in the Hot Cell Laboratory at STUDSVIK. The main objective of this initial step is to wash away any pre-oxidized phases formed during air storage in cell by exposing them to relatively high $NaHCO_3$ concentrations. Figure 3-1 show the collected fuel fragments and a leaching flask with the fuel immersed in the leaching solution.

Figure 3-1: Spent fuel samples used for dissolution experiments of STUDSVIK. One batch of fuel fragments (left image) and leaching flask containing fuel samples (right image).



The washing step was divided into a total of five contact periods as shown in Table 3-1. At the end of each contact period the glass baskets containing the fuel were transferred into a new flask containing fresh leaching solution. Samples of the leaching solution at the end of each contact period were centrifuged for 1h at 74 000 g.

Table 3-1: Contact periods for the washing step in experiments with SNF samples 5A2 (standard UOx fuel) and C1(Al-Cr-doped UOx fuel).

Contact period	Duration [days]	Cumulative duration [days]
1	1	1
2	5	6
3	8	14
4	20	54
5	71	105

Thereafter the samples were preserved in either 1% HNO_3 or 0.5% TMAH for analysis by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for masses 82-254 and I-129 respectively and gamma spectrometric analysis for Cs-137 determination. In-115 and Bi-209 are used as internal standards for the ICP-MS analysis.

After fulfillment of the criteria for a successful washing, both fuels were introduced in stainless-steel autoclaves with an inner quartz vessel that contains the leaching solution and peek internals. The sampling system consist of an internal PEEK line with a quartz filter (P4

10-16 µm pore size). The external line is made of stainless steel with two valves in series. Figure 3-2 show an example of the internal and external parts of the autoclaves.

Figure 3-2: Autoclave used in dissolution experiments with SNF under 55 bars hydrogen overpressure. Autoclave internals (left image) and exterior of the autoclave (right image).

Prior to assembling the autoclaves the free internal volume was determined for gas phase calculations obtaining a value of 950 cm^3. Leak tests were also performed by pressurizing the autoclaves with 50 bar of He and monitoring the pressure through 1 month. The pressure drop rate found was ~ 0.16 bar/month.

The autoclave vessels were filled with 680 ml of simplified groundwater, consisting of 10 mM NaCl and 2 mM $NaHCO_3$. Prior to loading, the autoclaves were sparged during 30 min with argon to minimize the air content. After loading the quartz baskets containing the fuel, the autoclaves were closed and sparged for another hour before the argon flow was stopped. Thereafter the autoclaves were pressurized up to the target pressure of 55 bar of H_2. No replenishment of gas due to pressure loss during the experiment is planned.

The concentration of fission products and actinides in the autoclave solution will be followed for ~2 years by 9 sampling points (liquid and gas sampling). The sample solutions are analysed in the same way as the solutions from the washing experiments. In addition, the composition of the gas phase is analysed by Gas-MS to detect air intrusion or release of fission gas from the fuel samples. The status of the planned sampling points is presented in Table 3-2.

Each sample point is taken in triplicate. The first sample (A) is used to rinse the sampling system and it is not analysed. Samples B and C are centrifuged at 74 000 g during one hour and thereafter the supernatant is removed and preserved as described above for the pre-wash samples.

Table 3-2: Autoclave sampling points in dissolution experiments with SNF under 55 bars hydrogen overpressure. Samples already taken and analysed are marked with an "✓".

Sampling point	Leaching time [days]	Liquid sample	Gas sample
1	0.1	✓	x
2	1	✓	✓
3	7	✓	✓
4	28	✓	✓
5	91	✓	✓
6	203	✓	✓
7	365	June 2019	June 2019
8	670	April 2020	April 2020
9	730	June 2020	June 2020

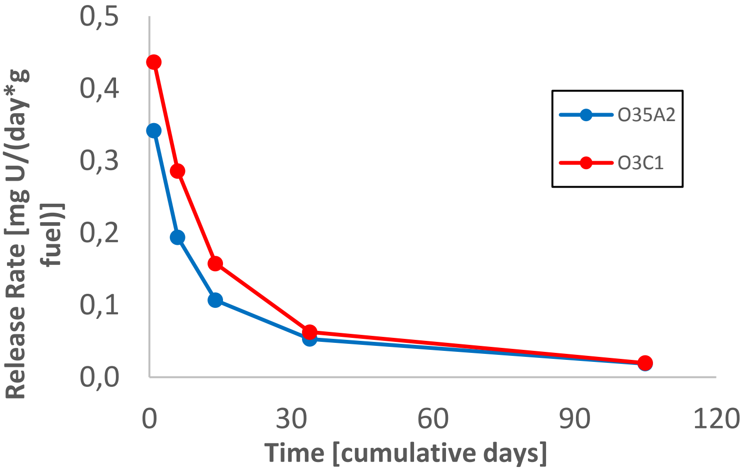
3.2 Results and discussion of studies with irradiated BWR UO_X fuels at STUDSVIK

It must be noted that the results presented are preliminary and therefore subjected to minor changes or adjustments.

3.2.1 Washing step

The uranium release rate is plotted against cumulative time in Figure 3-3. It can clearly be seen how the uranium release rate decreases markedly with washing time. After ~3 months both fuels exhibit considerably low and identical uranium release rates.

Figure 3-3: Uranium release rate as a function of time during the pre-wash of SNF samples 5A2 (standard UOx fuel) and C1(ADOPT / Al-Cr-doped UO_x fuel). "O35A2" denotes the standard UOx fuel and "O3C1" the ADOPT fuel.



3.2.2 Leaching under H_2 atmosphere

The initial pH and carbonate concentration were measured obtaining 8.2 and 2 mM respectively.

Tables 3-3 and 3-4 summarize the evolution of the composition of the gas phase in the two autoclaves.

Table 3-3: Pressure and gas composition autoclave O35A2 (standard UO_x fuel)

O35A2	Gas	G1	G2	G3	G4	G5
(Std. UO_2)	Kr [%]	0.000	0.000	0.000	0.000	0.000
	Xe [%]	0.000	0.000	0.001	0.001	0.002
	H_2 [%]	98.071	97.605	97.040	97.031	96.995
	He [%]	0.113	0.522	1.015	1.029	1.0584
	N_2 [%]	0.010	0.011	0.016	0.023	0.033
	O_2 [%]	0.006	0.006	0.006	0.007	0.007
	Ar [%]	1.800	1.856	1.920	1.909	1.904
Autoclave Pressure	[bar]	50.23	43.54	35.19	31.28	27.57
Duration	[days]	1	6	34	91	211

Table 3-4: Pressure and gas composition autoclave O3C1 (ADOPT fuel)

O3C1	Gas	G1	G2	G3	G4	G5
(ADOPT)	Kr [%]	0.000	0.000	0.000	0.000	0.000
	Xe [%]	0.000	0.000	0.001	0.001	0.001
	H_2 [%]	98.901	98.228	98.695	97.562	97.435
	He [%]	0.056	0.274	0.724	0.847	0.934
	N_2 [%]	0.010	0.011	0.014	0.017	0.023
	O_2 [%]	0.006	0.006	0.006	0.006	0.008
	Ar [%]	1.027	1.481	1.560	1.567	1.598
Autoclave Pressure	[bar]	49.02	43.77	37.72	34.41	31.98
Duration	[days]	1	6	34	91	211

The Kr and Xe results are close or below the limit of quantification. However, from the first leaching month, the isotopic composition of Xe in the gas phase matches fairly well the Xe inventory in the fuel. This implies that fission gas is released to some extent from both samples. Preliminary calculations indicate that 5.0% of the Xe inventory is released for the standard UO_x fuel and 3.8% for ADOPT.

Preliminary results of a number of radionuclides of interest from the aqueous phase of both autoclaves are summarized in Figure 3-4 and 3-5.

Figure 3-4: Aqueous concentrations of studied actinides as a function of leaching time experiments performed with standard UO$_x$ fuel (O35A2; left diagram) and ADOPT (O3C1; right diagram).

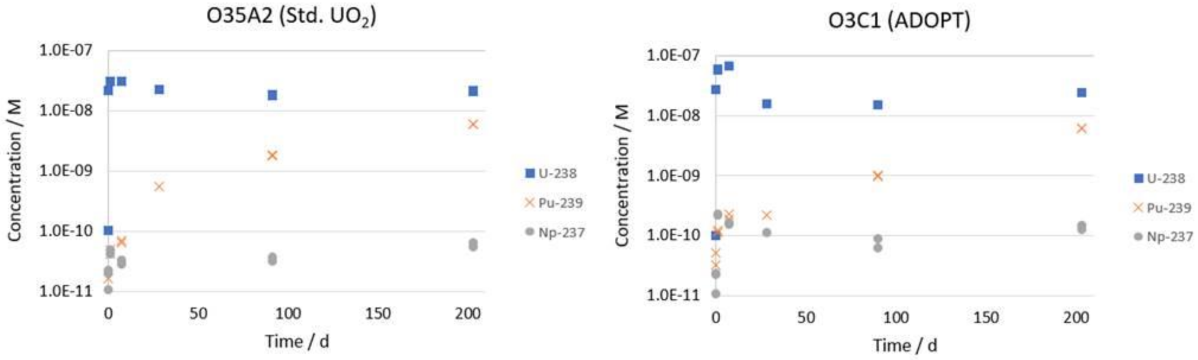
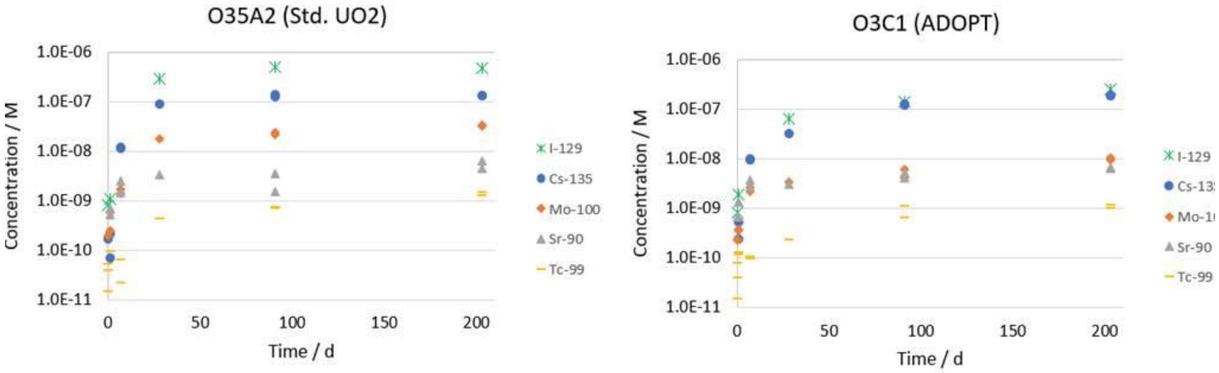


Figure 3-5: Aqueous concentrations of studied I-129, Cs-135, Mo-100, Sr-90 and Tc-99 as a function of leaching time experiments performed with standard UO$_x$ fuel (O35A2; left diagram) and ADOPT (O3C1; right diagram).



As can be seen in Figure 3-4, the initial rise of U-238 concentration in both autoclaves (due to dissolution of oxidized fuel layers as a result of air exposure during the transfer from the pre-wash to the autoclaves) is followed by a slow decrease attributable to reduction by H_2. For both autoclaves, the U-238 concentration after 208 days seems to stabilize at 1-2x10^{-8} M , slightly higher than the solubility for amorphous UO_2 (2-5x10^{-9} M) [5]. One possible explanation for this behaviour is the formation of nanosized U-Si colloids within the autoclave leaching solution. Further analysis are being considered to elucidate this potential explanation. Relative low concentrations for Pu and Np are observed in both cases (~ 3x10^{-10} for Np-137 and ~ 6x10^{-9} for Pu-239), although one order of magnitude higher than values reported by a previous study [6].

Highly soluble nuclides such as I-129 and Cs-137 increased steadily during the first month reaching a relative constant level for the standard UO_2 fuel. The ADOPT specimen is also rapidly transiting to near-constant concentrations however an increasing trend is still observed. The major release of other elements of interest such as Mo-100, Sr-90 and Tc-90 occurs within a few days, slowly approximating a constant value.

The largest difference between both fuels can be observed in the leaching behaviour of I-129. The FIAP (Fraction of Inventory in Aqueous Phase) after 6 months for the standard UO_2 fuel is 6.7 % while for ADOPT is 3.2 %. This difference can be explained given the larger grain size in ADOPT fuel, decreasing fission gas diffusion through the fuel and therefore reducing the FGR and the release of volatile elements during reactor operation such as I-129.

Furthermore, comparing the release of fission gases for standard UO_2 and ADOPT (Xe, 5.0% and 3.8% respectively) and I-129 (6.7% and 3.2%) a ratio of ~ 1:1 was observed for both autoclaves. This is in very good agreement with previous observations in a previous study by other authors [9].

At this point in the experiment, radionuclide concentrations are within the expected range when compared to previous leaching studies under hydrogen atmosphere [6, 8-10]. In addition, the overall doping effect on the leaching behaviour seem to be small.

4 Initial results of dissolution experiments with irradiated PWR UO_x fuel (73 $MWd/kg_{(HM)}$) performed by EURECAT

Within WP3 of DisCo, EURECAT in conjunction with UPC is contributing with three dissolution experiments on a PWR UO_x fuel with a local burnup of 73 $MWd{\cdot}(kg_{HM})^{-1}$. Initial results of the experiment “73YCWCa” performed with a cladded segment in “Young Cement Water with Calcium” (YCWCa) under oxic conditions are presented in this report. Two following experiments with cladded segments of the same fuel rod will be performed under Ar atmosphere. For comparison, details of a dissolution experiment (“73BIC”) with a similar SNF sample used in another project and leached in diluted NaCl solution with $NaHCO_3$ are also included in this report. Each SNF sample was obtained by cutting precisely through a pellet to obtain a segment without the interface between pellets. Further details about the SNF samples 73BIC and 73YCWCa are given in Table 1-1 and in Table 4-1.

Table 4-1: Characteristic properties of cladded SNF segments used in dissolution experiments 73YCWCa and 73BIC.

Sample	73YCWCa	73BIC
Length (mm)	2.9 ± 0.1	4.3 ± 0.1
Weight, only fuel (g)	1.779 ± 0.05	2.623 ± 0.05
Diameter without cladding (mm)	9.1 ± 0.1	9.1 ± 0.1
Surface area (mm^2)	460 ± 10	460 ± 10
^{235}U enrichment (weight%)	3.95	3.95
Grain size (µm)	6.4	6.4
Fission Gas Release (%)	13.6	13.6
Average Linear Power Density ($W{\cdot}cm^{-1}$)	255	255

4.1 Experimental and analytical details of dissolution studies with irradiated PWR UOx fuels performed by EURECAT

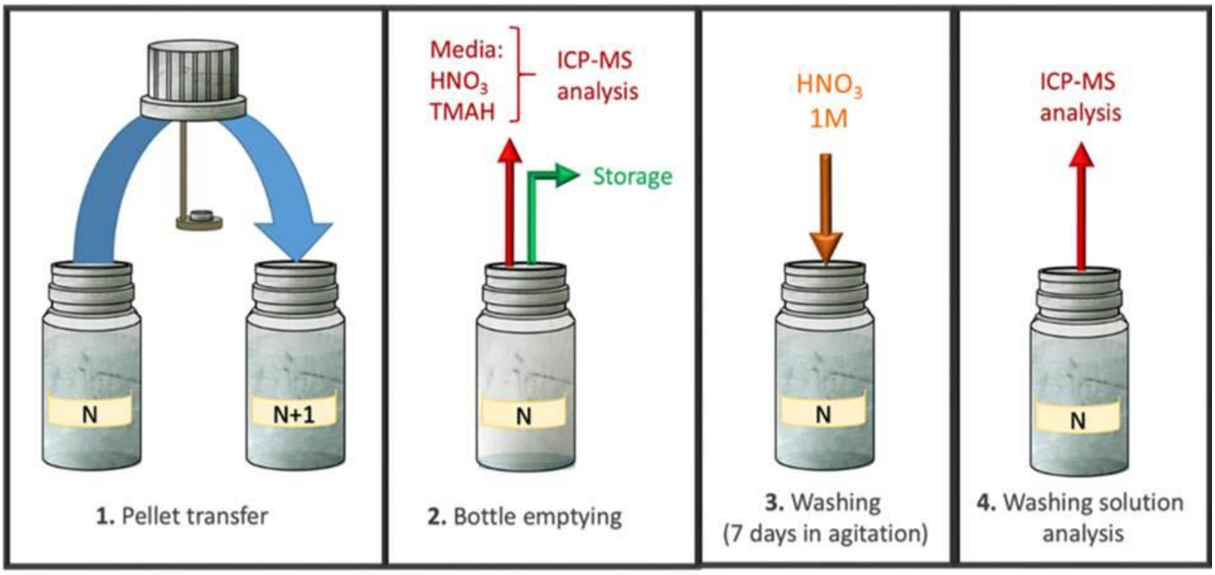
Based on the theoretical composition of the YCWCa, a simulated cement water was prepared as leachant, whose composition is shown in Table 4-2, together with NaCl-BIC solution of experiment 73BIC.

The methodology of the experiment followed a protocol reported in a previous study [12], in which the cladded segment was in contact with a leaching solution during different time intervals. Then, the cladded segment was transferred into the next bottle containing a fresh synthetic solution. After this, several aliquots were diluted in HNO_3 or tetramethylammonium hydroxide (TMAH) 1 wt. % to be analysed by ICP-MS. The emptied bottle was refilled with HNO_3 1 M and agitated during 7 days. This washing was done to remove any element that could have been adsorbed onto the plastic walls of the bottle during the first leaching step. Finally, a sample of this HNO_3 rinsing solution was taken to be analysed by ICP-MS (Figure 4-1).

Table 4-2: Composition of major ions present in YCWCa and NaCl-BIC type solutions used in two dissolution experiments with cladded segments of a PWR UO_x fuel with a local burnup of 73 MWd·(kg $_{HM}$)$^{-1}$.

Solution	pH	Na^+ (mMol·L^{-1})	Ca^{2+} (mMol·L^{-1})	Cl^- (mMol·L^{-1})	SiO_3^{2-} (mMol·L^{-1})	CO_3^{2-} (mMol·L^{-1})	OH^- (mMol·L^{-1})
73YCWCa	*13.4*	*5.0E+2*	*9.8E-1*	–	*2.0E+2*	*2.5E0*	*2.5E+2*
73BIC	*7.4*	*2.0E+1*	–	*1.9E+1*	–	*1.0E0*	*2.5E-7*

Figure 4-1: Solution sampling procedure in dissolution experiments73YCWCa and 73BIC.



4.2 Results and discussion of studies with irradiated PWR UO_X fuels performed by EURECAT

Preliminary results include 10 samples that have been partially analysed. Some relevant radionuclides (U, Rb, Sr, Mo, Tc, Cs, I) have been selected. Cumulative moles and Cumulative Fraction of Inventory in Aqueous Phase (CFIAP) results are shown in Figure 4-2 for the experiment 73YCWCa.

The trend is a faster dissolution at the beginning and a slower dissolution after the first week. I, Cs, Mo and U present the highest values of cumulative moles. This behaviour was observed for Cs and U in previous experiments, but it is relevant that this was not observed neither for Mo nor Tc in water with a lower pH. In Figure 4-3, the Instant Release Fraction of Cs (IRF_{Cs}) measured in experiment 73YCWCa, which is conducted at pH 13.4, is compared to IRF_{Cs} measured in experiment 73BIC performed at near neutral pH.

Further speciation studies are required for both, U and Sr. On the other hand, a higher RN release can be observed for every studied element (excluding Sr), which can be attributed to a greater initial dissolution of the UO_2 matrix. The amount of dissolved Mo and Tc is significantly higher than for 73BIC segment (Table 4-3).

Figure 4-2: Measured release of Cs, I, Mo, Rb, Sr, Tc and U as a function of leaching time in the experiment with cladded segment 73YCWCa. Cumulative moles are shown in the left diagram, CFIAP (%) values are shown in the rigt diagram.

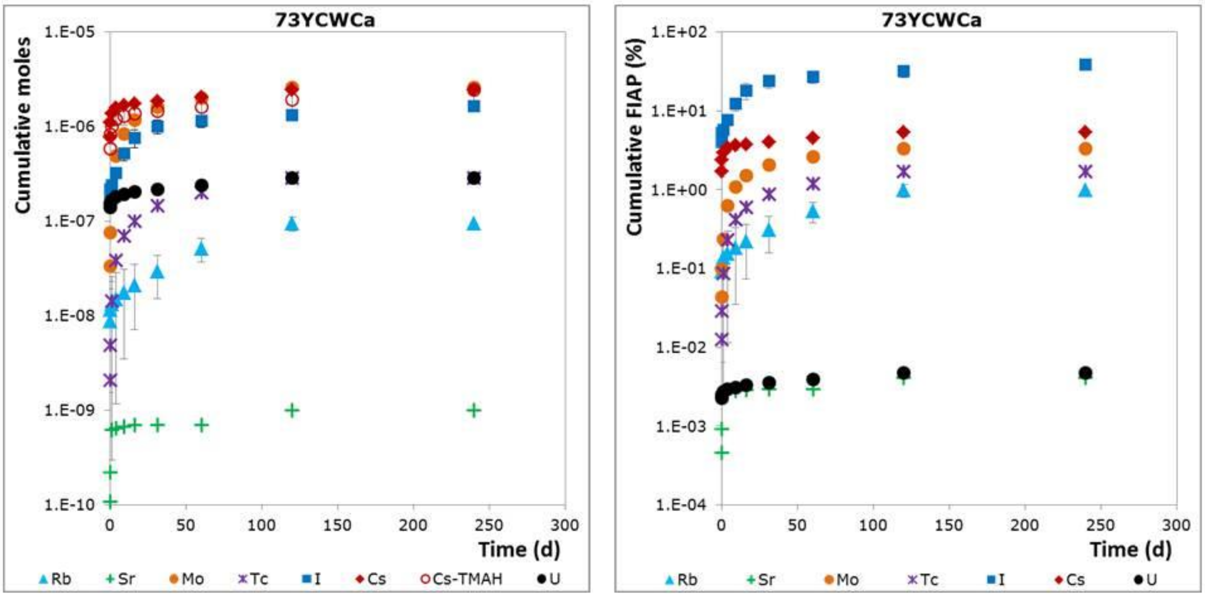


Figure 4-3: Instant Release Fraction (%)for Cs: comparison of 73YCWCa and 73BIC experiments.

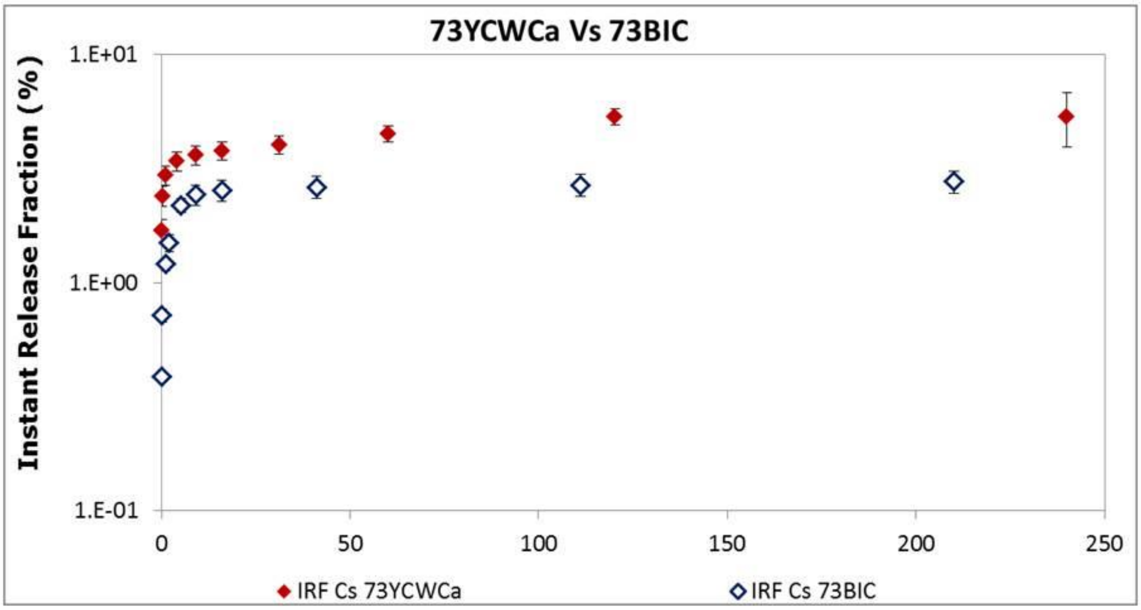


Table 4-3: IRF results for 73YCWCa and 73BIC.

IRF (%)	pH	Cs	I	Mo	Tc	Rb	Sr
73YCWCa	13.4	5.3±0.6	39±6	3.3±0.3	1.7±0.2	1.0±0.2	b.d.l.
73BIC	7.4	2.7±0.3	-	<0.005	0.011±0.005	0.3±0.1	0.09±0.01

Note: b.d.l. means Below Detection Limit.

5 Dissolution experiments with irradiated PWR UO_x fuel (58 MWd/kg$_{(HM)}$) and irradiated PWR MOX fuel (54 MWd/kg$_{(HM)}$) performed by JRC-KA

JRC-KA is contributing to WP3 of DisCo with experimental studies of the long-term stability of an irradiated Cr_2O_3-doped UO_x fuel (58 MWd·(kg $_{HM}$)$^{-1}$) and a spent MOX fuel (54 MWd·(kg $_{HM}$)$^{-1}$) in diluted NaCl solution with $NaHCO_3$ under anoxic and reducing conditions. Not only leachates and solid after leaching, but also the gas phase will be analysed in order to obtain a more complete description of the redox conditions and of the processes affecting the evolution of the system.

Within WP2 of DisCo, the irradiated MOX sample has been selected from the agreeing γ-scan and burn-up profiles. The sample was cut and are stored under Ar in under-pressure awaiting the dissolution experiment. The irradiated Cr_2O_3-doped UO_x fuel was cut according to the cutting plan. Details about the sample preparation are given by Farnan et al. [3]. Both types of fuel samples are scheduled for dissolution and inventory determination.

Since both dissolution studies are going to be performed for strongly reducing conditions (i.e. hydrogen overpressure), autoclaves will be used as reaction vessels in these experiments. At the final leak rate test before introducing a first autoclave into hot cell Z112 it was discovered that some of the used Titanium cutting rings from the company Swagelok were cracked. As a consequence, the final safety acceptance protocol could not be signed and the hot cell autoclave is not cleared for hot cell use. The onset of the dissolution experiments has been postponed to the second half of 2019 due to the technical problems with the cutting rings and renovation of dissolution cell Z105 at JRC-KA.

6 References

[1] V. Metz, E. Bohnert, C. Bube, E. González-Robles, B. Kienzler, A. Loida, N. Müller, P. Carbol, J.-P. Glatz, R. Nasyrow, D. Papaioannou, V.V. Rondinella, D. Serrano Purroy, D. Wegen, H. Curtius, M. Klinkenberg, I. Günther-Leopold, C. Cachoir, K. Lemmens, T. Mennecart, J. Vandenborre, I. Casas, F. Clarens, J. de Pablo, R. Sureda Pastor, Z. Hózer, E. Slonszki, E. Ekeroth and O. Roth (2012). *Characterisation of spent nuclear fuel samples to be used in FIRST-Nuclides – relevance of samples for the Safety Case,* Deliverable No. 1.1 of the CP FIRST-Nuclides, Karlsruhe, Germany.

[2] V. Metz, E. González-Robles, N. Müller, E. Bohnert, M. Herm, M. Lagos, B. Kienzler, D. Serrano-Purroy, J.Y. Colle, O. Beneš, F. Naisse, T. Wiss, R.J.M. Konings, D.H. Wegen, D. Papaioannou, R. Gretter, R. Nasyrow, V.V. Rondinella, J.-P. Glatz, H. Curtius, H.W. Müskes, N. Like, D. Bosbach, I. Günther-Leopold, E. Curti, A. Froideval Zumbiehl, H.P. Linder, K. Govers, M. Verwerft, W. Van Renterghem, K. Lemmens, T. Mennecart, C. Cachoir, L. Adriaensen, A. Dobney, M. Gysemans, J. Vandenborre, A. Traboulsi, G. Blain, J. Barbet, M. Fattahi, R. Sureda Pastor, E. Slonszki, Z. Hózer and O. Roth (2013). *Characterisation of spent nuclear fuel samples and description of methodologies and tools to be applied in FIRST-Nuclides,* Deliverable No. 1.2 of the CP FIRST-Nuclides, Karlsruhe, Germany.

[3] I. Farnan, D. Bosbach, D. Wegen, E. Gonzalez-Robles Corrales, C. Jegou, C. Corkhill, D. I. Hambley, J. Cobos Sabate (2018). *Initial state report: sample characterisation and experimental set-up,* Deliverable No. 2.1 of the H2020-project DisCo, Cambridge, United Kingdom.

[4] J. Arborelius, K. Backman, L. Hallstadius, M. Limbaeck, J. Nilsson, B. Rebensdorff, G. Zhou, K. Kitano, R. Loefstroem, G. Roennberg (2006) *Advanced doped UO_2 pellets in LWR applications*, J. Nucl. Sci. Technol., 43, 967-976.

[5] B. Kienzler, V. Metz, A. Valls (2014) Proceedings of 7th EC FP – FIRST-Nuclides Final Workshop, Karlsruhe, Germany, *KIT Scientific Reports 7716*, p. 276, http://dx.doi.org/10.5445/KSP/1000054569.

[6] R. Guillamont et al. (2003) *Update on the chemical thermodynamics of U, Np, Pu, Am and Tc*, OECD NEA, Elsevier

[7] A. Puranen, O. Roth, L.Z. Evins, K. Spahiu (2018), *Aqueous leaching of high burnup UO_2 fuel under hydrogen conditions*, MRS Advances 3(19), 1013-1018

[8] E. González-Robles, M. Fuß, E. Bohnert, N. Müller, M. Herm, V. Metz, B. Kienzler (2015) Study of the release of the fission gases (Xe and Kr) and the fission products (Cs and I) under anoxic conditions in bicarbonate water. *Materials Research Society, Scientific Basis for Nuclear Waste Management,* Mat. Res. Symp. Proc. 1744, 283-289.

[9] P. Fors, P. Carbol, S. Van Winkel, K. Spahiu (2009), *Corrosion of high burn-up structured UO_2 fuel in presence of dissolved H_2,* J. Nucl. Mater. 394, 1-8.

[10] A. Loida, V. Metz, B. Kienzler, H. Geckeis (2005), *Radionuclide release from high burnup spent fuel during corrosion in salt brine in the presence of hydrogen overpressure,* J. Nucl. Mater. 346, 24-31.

[11] K. Spahiu, D. Cui, M. Lundström (2004) *The reduction of U(VI) by near field hydrogen in the presence of UO_2(s),* Radiochim. Acta, 92, 625-629.

[12] E. González-Robles, D. Serrano-Purroy, R. Sureda, I. Casas, J. de Pablo (2015) *Dissolution experiments of commercial PWR (52 MWd/kgU) and BWR (53 MWd/kgU) spent nuclear fuel cladded segments in bicarbonate water under oxidizing conditions. Experimental determination of matrix and instant release fraction.* J. Nucl. Mater., 465, 63-70.