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Spent nuclear fuel experiments: Dissolution results for modelling input

Authors: V. Metz, M. Herm (KIT-INE); F. Clarens, J. Kokinda, J. de Pablo (EURECAT / UPC); P. Carbol, D. Serrano-Purroy (JRC-KA), A. Barreiro, O. Roth (STUDSVIK)

Editor: V. Metz (KIT-INE)

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1 Introduction

The EURATOM H2020-project DisCo (*Modern spent nuclear fuel Dissolution in failed container Conditions*) focuses on the dissolution of spent nuclear fuel (SNF) 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 developed to enhance our understanding of these modern fuels in comparison with traditional nuclear fuels, so-called "standard UO_x fuels".

This progress report summarizes the experimental results gained in Work Package 3 of DisCo until the third year of the project (June 2020). The main goal of WP3 is to study experimentally the dissolution of spent UO_x fuels containing dopants as well as the dissolution of spent MOX fuels under relevant disposal conditions. The research groups that contribute with experiments to WP3 are 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). All partners of WP3 dealt with spent nuclear fuel, which had been irradiated in light water nuclear reactors. Characteristic data of these spent UO_x fuels and spent MOX fuels are given in Table 1. Since there were delays in the sample preparation of the fuel samples and technical problems with the experimental set-ups of EURECAT and JRC-KA, start of some of their experiments is expected in the second half-year of 2020.

Table 1: Characteristic data of spent UO_x fuels and spent MOX fuels used in DisCo WP3 dissolution experiments.

sample name	**fuel type**	**reactor type**	**initial enrich-ment**	**average burn-up [MWd/kg]**	**local burn-up [MWd/kg]**	**linear power [W/cm]**
MOX-H	MOX	PWR	5.54% Pu	54	56	180
KWU11.38-5810	MOX	PWR	3.2% Pu	38	*not given*	200
KWU11.38-5810	MOX	PWR	3.2% Pu	38	*not given*	200
5A2	standard UOx	BWR	3.5% U-235	57	62.9	*not given*
C1	Al-Cr-doped UOx	BWR	4.1% U-235	59	65.9	*not given*
73BIC	standard UOx	PWR	4.0% U-235	60	73	255
73YCWCa	standard UOx	PWR	4.0% U-235	60	73	255

In the following sections preliminary results of the dissolution experiments with irradiated UO_x and MOX fuels performed by JRC-KA, KIT-INE and STUDSVIK under reducing conditions, as well as by EURECAT dissolution experiments with an irradiated UO_x fuel under oxic conditions are presented in this progress report. Digital data sheets with results of the respective experiments have been provided to partner institutions of Work Package 5 for input of their modelling studies in June 2020. It is emphasized that the experimental results reported in this deliverable are preliminary and may therefore be subjected to changes or adjustments in continuation of the DisCo project.

2 General aspects of the dissolution experiments and compiled data

Current experiments are performed with two BWR UO_x fuels having burnups of 57 and 59 $MWd\cdot(kg_{HM})^{-1}$ as well as with two PWR MOX fuels having burnups of 38 and 54 $MWd\cdot(kg_{HM})^{-1}$ (average burnups). In five autoclave experiments, fragments and cladded segments of these irradiated fuel samples were exposed to diluted NaCl solution with 1 to 10 mM $NaHCO_3$ (pH ~ 8, denoted as NaCl-BIC) under anoxic to strongly reducing conditions. Moreover, two dissolution experiments with a PWR UO_x fuel, having a local burnup of 73 $MWd\cdot(kg_{HM})^{-1}$, had been conducted under oxic conditions in NaCl-BIC type solution and in so-called "Young Cement Water with Calcium" (denoted as YCWCa), which is a hyper-alkaline diluted NaOH, $Ca(OH)_2$ solution, containing 77 mM Na_2CO_3 and other minor constituents.

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 $MWd\cdot(kg_{HM})^{-1}$ local burnup had been prepared already before the onset of DisCo. Preparation of cladded segments and fragments from PWR MOX fuel with a burn-up of 38 and 54 $MWd\cdot(kg_{HM})^{-1}$ were performed in the framework of Work Package 2 of DisCo. Diluted NaCl solution with 1 to 2 mM $NaHCO_3$ (pH ~ 8, denoted as NaCl-BIC) and "Young Cement Water with Calcium", are used in the dissolution experiments as leachant (Table 2). Most dissolution experiments are conducted under anoxic to strongly reducing conditions in presence of hydrogen, argon/hydrogen or argon/CO_2 atmospheres. Partial pressures of hydrogen and argon are in the range of 3 to 55 bars. Additionally, two experiments with a PWR UO_x fuel of 73 $MWd\cdot(kg_{HM})^{-1}$ local burnup had been conducted in air and in the meantime terminated. Sample types, fission gas release measured in puncturing tests, cooling time prior to dissolution experiments, solution types and gas atmospheres of dissolution experiments with spent UO_x fuels and spent MOX fuels are reported in Table 2.

Preliminary results of the dissolution experiments with irradiated UO_x and MOX fuels performed by JRC-KA, KIT-INE and STUDSVIK under anoxic and strongly reducing conditions, as well as by EURECAT dissolution experiments with an irradiated UO_x fuel

under oxic conditions are presented in this progress report. Digital data sheets with results of the respective experiments have been provided to partner institutions of Work Package 5 for input of their modelling studies in June 2020. Results on actinides and fission products released into solution are reported in molar concentrations. Furthermore, concentrations of fission gases and partial pressures of hydrogen and oxygen, measured during the dissolution experiments of KIT-INE and STUDSVIK, are presented.

Table 2: Sample types, fission gas release measured in puncturing tests, cooling time prior to dissolution experiments, solution types and gas atmospheres of dissolution experiments with spent UO_x fuels and spent MOX fuels.

sample name	**sample type**	**fission gas release in puncturing test**	**cooling time [years]**	**solution**	**main gas phase**
MOX-H	cladded segment	2.5%	17	NaCl-BIC	Ar 32 bars
KWU11.38-5810	fragments	6.0%	32	NaCl-BIC	H2 3 bars
KWU11.38-5810	cladded segment	6.0%	32	NaCl-BIC	H2 3 bars
5A2	fragments	2.5%	12	NaCl-BIC	H2 55 bars
C1	fragments	1.4%	12	NaCl-BIC	H2 55 bars
73BIC	cladded segment	13.6%	15	NaCl-BIC	air
73YCWCa	cladded segment	13.6%	15	YCWCa	air

It is emphasized that the experimental results, reported in this deliverable, represent the state of the experimental works in June 2020 and the reported data are considered preliminary. Therefore, these data may be subjected to changes or adjustments in continuation of the DisCo project.

3 Dissolution experiment with 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 a spent MOX fuel (denoted as MOX-H) with a local burn-up of 56 MWd·(kg $_{HM}$)$^{-1}$. In this autoclave experiment, a cladded segment is exposed to diluted NaCl solution with $NaHCO_3$ under anoxic conditions. Details about the preparation of the MOX segment, its theoretical inventory and details of the experimental set-up are reported by Serrano Purroy et al. [1]. In the following, relevant experimental conditions and preliminary results of radionuclides released into the aqueous phase of leaching are presented.

3.1 Details of the dissolution experiment with PWR MOX fuel (54 MWd/kg$_{(HM)}$)

The dissolution test is performed in an experimental set-up of autoclaves manufactured from non-reductive materials (mainly Ti and PEEK). The experimental set-up consists of an ‘experiment autoclave’, located inside a hot-cell, and a ‘refill autoclave’ located in a glovebox outside of the hot-cell from which solution can be transferred via gas tubes into the ‘experiment autoclave’. Filling and refilling of solution and gas in the ‘experiment autoclave’ is driven by difference in gas pressure between the ‘refill autoclave’ and the ‘experiment autoclave’. For refilling solution from the ‘refill autoclave’ to the ‘experiment autoclave’ a 5-10 bar higher pressure is needed in the ‘refill autoclave’.

The experiment with the spent MOX sample started at the 8th of October 2019 at an initial pressure of 32 bars under anoxic conditions (Ar / 0.003% CO_2) using approximately 110-120 mL of simplified NaCl-BIC groundwater (1 mM $NaHCO_3$ and 19 mM NaCl). The experimental temperature corresponds to standard hot-cells working conditions: 25±5 °C. At the beginning of the experiment, two complete solution replenishments were carried out over two consecutive days. This was done to minimize contribution from existing pre-oxidized phases. After the second replenishment, the solution was not any more renewed after the samplings, to minimize introduction of oxygen into the autoclave system. Samples were taken at regular intervals. In all samplings, at the initial complete replenishments or later under static conditions, both acidified and non-acidified samples were taken. Each complete set of sampling corresponds to a reduction in volume and pressure inside the autoclave of approximately 6-8 mL and 3-4 bar, respectively.

3.2 Results of the dissolution experiment with PWR MOX fuel (54 MWd/kg$_{(HM)}$)

In June 2020, aqueous concentrations of actinides (Am, Cm, Np, Pu and U) and of selected fission products (Cs, Mo, Tc and Zr) were reported for an experimental duration of the first 48 days of dissolution experiment MOX-H (Table 3).

Table 3*: Aqueous concentrations of actinides (Am, Cm, Np, Pu and U) and fission products (Cs, Mo, Tc and Zr) in experiment MOX-H.*

time (days)	uranium concentration (mol L^{-1})	plutonium concentration (mol L^{-1})	neptunium concentration (mol L^{-1})	americium concentration (mol L^{-1})	curium concentration (mol L^{-1})
0.2	4.8E-07	2.2E-09	1.2E-10	1.7E-10	7.6E-12
1	6.5E-07	3.2E-09	1.7E-10	3.9E-10	1.8E-11
3	9.2E-07	6.1E-09	2.5E-10	1.0E-09	4.4E-11
13	1.3E-06	5.0E-09	3.4E-10	8.3E-10	4.3E-11
48	2.5E-06	5.6E-09	5.4E-10	9.0E-10	5.1E-11

time (days)	technetium concentration (mol L^{-1})	molybdenum concentration (mol L^{-1})	zirconium concentration (mol L^{-1})	cesium concentration (mol L^{-1})
0.2	4.0E-09	8.7E-08	1.2E-09	3.8E-06
1	6.1E-09	1.1E-07	1.7E-09	4.0E-06
3	8.6E-09	1.3E-07	3.8E-09	4.1E-06
13	1.4E-08	1.7E-07	2.6E-09	4.2E-06
48	2.8E-08	3.3E-07	2.2E-09	4.3E-06

4 Dissolution experiments with irradiated PWR MOX fuel (38 MWd/kg$_{(HM)}$) performed by KIT-INE

Within WP3 of DisCo, studies by KIT-INE provide experimental data concerning the matrix dissolution of an irradiated PWR MOX fuel (denoted as KWU11.38-5810, with an average burn-up of 38 MWd·(kg $_{HM}$)$^{-1}$) under strongly 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 are currently conducted in the shielded box-line of KIT-INE with periodical sampling campaigns of the gaseous and the aqueous phase. Details about characteristics of the spent nuclear fuel samples, their irradiation history, experimental conditions and analytical methods are given by Herm et al. [2]. In the following, relevant experimental conditions and preliminary results of radionuclides released into the aqueous phase up to almost two years of leaching are presented.

4.1 Details of the dissolution experiments with irradiated PWR MOX fuel (38 MWd/kg$_{(HM)}$)

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 NaCl-BIC type solution, 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 dissolution experiments were started. 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.

4.2 Results of the dissolution experiments with irradiated PWR MOX fuel (38 $MWd/kg_{(HM)}$)

In the two dissolution experiments with a cladded segment and fragments of irradiated MOX sample KWU11.38-5810 aqueous concentrations of actinides (Am, Cm, Np, Pu and U) and of selected fission products (Cs, I, Sr and Tc) were analysed for an experimental duration of 370 and 364 days, respectively (reported status June 2020). Concentrations of these elements measured in the experiment with the cladded segment are given in Table 4 and those measured in the experiment with the fragments are given in Table 5. Additionally, concentrations of Kr and Xe released into the gas phase are reported as fission gas release values in Table 6.

Table 4*: Aqueous concentrations of actinides (Am, Cm, Np, Pu and U) and fission products (Cs, I, Sr and Tc) in the experiment with a cladded segment of MOX sample KWU11.38-5810.*

time (days)	uranium concentration (mol L^{-1})	plutonium concentration (mol L^{-1})	neptunium concentration (mol L^{-1})	americium concentration (mol L^{-1})	curium concentration (mol L^{-1})
1	4.0E-06	4.7E-09	1.1E-09	4.2E-09	1.3E-10
2	4.0E-07	8.7E-10	1.5E-10	2.3E-10	2.5E-11
160	4.2E-08	1.6E-09	3.4E-11	5.0E-10	2.8E-11
370	2.2E-08	4.5E-10	2.2E-11	1.2E-10	2.6E-11

time (days)	technetium concentration (mol L^{-1})	strontium concentration (mol L^{-1})	cesium concentration (mol L^{-1})	iodine concentration (mol L^{-1})
1	n.g.	3.1E-09	6.2E-06	n.g.
2	n.g.	3.1E-10	8.4E-07	n.g.
160	9.8E-09	4.2E-08	4.3E-06	7.6E-06
370	4.5E-09	4.6E-08	4.4E-06	8.8E-06

Table 5*: Aqueous concentrations of actinides (Am, Cm, Np, Pu and U) and fission products (Cs, I, Sr and Tc) in the experiment with fragments of MOX sample KWU11.38-5810.*

time (days)	uranium concentration (mol L^{-1})	plutonium concentration (mol L^{-1})	Neptunium Concentration (mol L^{-1})	americium concentration (mol L^{-1})	curium concentration (mol L^{-1})
1	2.0E-06	2.8E-08	1.7E-09	3.7E-09	1.0E-10
2	1.3E-07	1.6E-09	8.4E-11	7.8E-10	4.6E-11
154	7.2E-08	4.5E-09	6.5E-11	1.1E-09	3.3E-11
364	1.5E-08	4.4E-10	1.7E-11	1.8E-11	1.9E-11

time (days)	technetium concentration (mol L^{-1})	strontium concentration (mol L^{-1})	Cesium Concentration (mol L^{-1})	iodine concentration (mol L^{-1})
1	n.g.	5.3E-09	4.5E-06	n.g.
2	n.g.	8.2E-10	2.6E-07	n.g.
154	7.5E-09	6.1E-09	1.1E-06	3.3E-06
364	4.0E-09	9.3E-09	1.5E-06	5.5E-06

Table 6: Measured hydrogen partial pressure and fission gas release during the dissolution experiments with irradiated *MOX fuel KWU11.38-5810*.

Experiment: KWU11.38-5810 segment		
time (days)	fission gas release (%)	pH_2 (bar)
1	0.39	3.2
2	n.g.	3.2
160	5.28	3.2
370	1.00	3.2
Experiment: KWU11.38-5810 fragments		
time (days)	fission gas release (%)	pH_2 (bar)
1	0.35	3.2
2	0.37	3.2
154	9.88	3.2
364	3.37	3.2

5 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 (denoted as 5A2) and an Al-Cr-doped UO_x fuel (denoted as C1), both irradiated in a BWR and achieving a similar average burnup (57 and 59 $MWd\cdot(kg_{HM})^{-1}$, respectively). In these two dissolution experiments under strongly reducing conditions, the behaviour of the irradiated ADOPT fuel is compared to the performance of the standard UO_2 fuel under the same experimental conditions. The two fuels have very similar power histories, having been irradiated in the same assembly.

The dissolution 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 [3,4]. Characteristic data of the studied SNF samples "5A2" (standard UO_x fuel) and "C1" (ADOPT UO_x fuel) experimental conditions and analytical methods are given by Barreiro-Fidalgo et al. [3] and Metz et al. [4].

5.1 Details of the dissolution experiments with irradiated BWR UOx fuels (57 and 59 $MWd/kg_{(HM)}$)

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 attempt to wash away any pre-oxidized phases that were presumable formed during air storage in the hot cell (approximately three years) by exposing them to relatively high $NaHCO_3$ concentrations. The washing step was divided into five contact periods. At the end of each contact period, the glass baskets containing the fuel were transferred into a new flask containing fresh leaching solution.

After the initial leaching period, both fuels were introduced in stainless-steel autoclaves with an inner quartz vessel that contains the leaching solution and PEEK internals. The sampling system consists of an internal PEEK line with a quartz filter. The external line is made of stainless steel with two valves in series. The autoclave vessels were filled with 680 ml of a NaCl-BIC type solution, 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. The concentration of radionuclides in the autoclave is monitored for a period of about two years. Besides analyses of the aqueous concentrations of the radionuclides, the composition of the gas phase is analysed by Gas-MS to detect air intrusion or release of fission gas from the fuel samples.

5.2 Results of dissolution experiments with irradiated BWR UOx fuels (57 and 59 MWd/kg$_{(HM)}$)

The investigation of STUDSVIK with two irradiated BWR UOx fuels provides the most comprehensive experimental data-set of work package 3. In June 2020, data were available for an experimental duration of 642 days. In the following aqueous concentrations of actinides (Am, Cm, Np, Pu and U) and fission products (Ba, Cs, Gd, I, Mo, Rb, Sr, Tc and Zr) are reported. Concentrations of these elements measured in the experiment 5A2 with fragments of the irradiated UOx fuel with a burn-up of 57 MWd/kg$_{(HM)}$ are given in Table 7 and those measured in the experiment with fragments of the irradiated UOx fuel with a burn-up of 59 MWd/kg$_{(HM)}$ are given in Table 8. Table [9] presents measured hydrogen and oxygen partial pressure as well as data on fission gas release during the dissolution experiments.

Table 7: Aqueous concentrations of actinides (Am, Cm, Np, Pu and U) and fission products (Ba, Cs, Gd, I, Mo, Rb, Sr, Tc, Zr) in experiment 5A2 with irradiated UOx fuel (57 MWd/kg$_{(HM)}$).

time (days)	uranium concentration (mol L^{-1})	plutonium concentration (mol L^{-1})	neptunium concentration (mol L^{-1})	americium concentration (mol L^{-1})	curium concentration (mol L^{-1})
0.1	2.2E-08	2.3E-11	2.1E-11	1.6E-12	2.1E-12
1	3.1E-08	8.4E-11	4.5E-11	4.2E-12	6.3E-12
7	3.1E-08	1.2E-10	3.1E-11	2.2E-11	1.4E-11
28	1.9E-08	7.1E-10	1.7E-11	9.5E-11	4.2E-11
91	1.8E-08	3.4E-09	3.5E-11	3.6E-10	2.4E-10
203	2.1E-08	1.0E-08	5.6E-11	9.1E-10	5.6E-10
421	2.6E-08	3.1E-08	1.4E-10	2.2E-09	1.3E-09
642	2.7E-08	4.5E-08	1.8E-10	2.9E-09	1.6E-09

time (days)	Ba conctr. (mol L^{-1})	Gd conctr. (mol L^{-1})	Tc conctr. (mol L^{-1})	Sr conctr. (mol L^{-1})	Mo conctr. (mol L^{-1})	Zr conctr. (mol L^{-1})	Rb conctr. (mol L^{-1})	Cs conctr. (mol L^{-1})	I conctr. (mol L^{-1})
0.1	6.4E-10	1.2E-11	4.6E-11	0.0E+00	0.0E+00	5.5E-10	0.0E+00	4.4E-10	2.5E-09
1	2.6E-10	1.6E-11	9.4E-11	0.0E+00	1.1E-09	7.7E-10	0.0E+00	2.3E-09	2.8E-08
7	3.1E-08	8.7E-11	4.4E-11	1.6E-09	5.1E-09	8.0E-10	3.7E-09	7.9E-08	-
28	4.4E-08	3.0E-10	1.5E-09	5.1E-09	5.5E-08	1.5E-09	2.0E-08	4.8E-07	2.9E-07
91	4.8E-08	1.4E-09	7.2E-10	5.0E-09	7.3E-08	8.5E-09	3.0E-08	8.3E-07	5.1E-07
203	5.6E-08	3.5E-09	1.4E-09	1.0E-08	1.1E-07	5.8E-08	1.6E-08	8.3E-07	4.7E-07
421	7.0E-08	6.0E-09	3.6E-09	1.3E-08	1.5E-07	1.4E-07	1.7E-08	8.6E-07	4.4E-07
642	7.6E-08	7.0E-09	2.7E-09	1.7E-08	1.4E-07	2.0E-07	1.6E-08	7.8E-07	7.9E-07

Table 8: Aqueous concentrations of actinides (Am, Cm, Np, Pu and U) and fission products (Ba, Cs, Gd, I, Mo, Rb, Sr, Tc, Zr) in experiment C1 with irradiated UOx fuel (59 MWd/kg$_{(HM)}$).

time (days)	uranium concentration (mol L^{-1})	plutonium concentration (mol L^{-1})	neptunium concentration (mol L^{-1})	americium concentration (mol L^{-1})	curium concentration (mol L^{-1})
0.1	2.7E-08	8.2E-11	2.3E-11	4.2E-12	3.7E-12
1	6.0E-08	2.2E-10	2.2E-10	9.4E-12	5.3E-12
7	6.8E-08	3.9E-10	1.6E-10	2.7E-11	2.0E-11
28	1.3E-08	2.3E-10	5.5E-11	2.8E-11	1.5E-11
91	1.5E-08	1.8E-09	7.6E-11	2.3E-10	1.8E-10
203	2.4E-08	1.1E-08	1.4E-10	8.0E-10	4.5E-10
421	4.0E-08	3.7E-08	3.6E-10	1.9E-09	1.1E-09
642	4.8E-08	6.6E-08	5.6E-10	3.1E-09	1.5E-09

time (days)	Ba conctr. (mol L^{-1})	Gd conctr. (mol L^{-1})	Tc conctr. (mol L^{-1})	Sr conctr. (mol L^{-1})	Mo conctr. (mol L^{-1})	Zr conctr. (mol L^{-1})	Rb conctr. (mol L^{-1})	Cs conctr. (mol L^{-1})	I conctr. (mol L^{-1})
0.1	1.1E-09	1.5E-11	5.9E-11	n.g.	n.g.	8.2E-10	n.g.	1.0E-09	2.5E-09
1	6.9E-09	4.1E-11	1.3E-10	n.g.	6.5E-10	9.7E-10	4.4E-10	2.6E-09	3.7E-09
7	3.8E-08	8.5E-11	1.0E-10	3.1E-09	8.4E-09	1.1E-09	7.1E-09	5.9E-08	n.g.
28	2.9E-08	1.5E-10	1.1E-09	2.5E-09	9.4E-09	7.8E-10	6.1E-09	1.7E-07	6.7E-08
91	3.8E-08	1.3E-09	8.8E-10	7.5E-09	1.6E-08	9.6E-09	1.1E-08	7.2E-07	1.5E-07
203	5.1E-08	3.5E-09	1.1E-09	1.2E-08	3.3E-08	7.3E-08	n.g.	1.1E-06	2.5E-07
421	7.3E-08	6.4E-09	3.5E-09	1.8E-08	4.4E-08	1.7E-07	n.g.	1.2E-06	2.9E-07
642	9.5E-08	8.5E-09	3.0E-09	2.3E-08	6.6E-08	2.9E-07	n.g.	1.2E-06	3.1E-07

Table 9: Measured hydrogen and oxygen partial pressure and fission gas release in experiments 5A2 and C1.

Experiment 5A2			
time (days)	fission gas release (%)	pO_2 (bar)	pH_2 (bar)
0.1	n.g.	n.g.	n.g.
1	0.50	0.003	45.3
7	0.30	0.002	39.3
28	4.30	0.002	31.2
91	4.9	0.002	28.1
203	6	0.002	24.8
421	6.5	0.002	22.4
642	7.7	0.001	22.0
Experiment C1			
time (days)	fission gas release (%)	pO_2 (bar)	pH_2 (bar)
0.1	n.g.	n.g.	51.0
1	n.g.	0.003	44.6
7	n.g.	0.002	39.7
28	1.66	0.002	33.6
91	2.12	0.002	31.0
203	4.32	0.002	29.0
421	8.00	0.002	26.9
642	8.07	0.002	26.5

6 Dissolution experiments with irradiated PWR UO_x fuel (73 $MWd/kg_{(HM)}$) performed by EURECAT

Up until June 2020, EURECAT contributed to WP3 of DisCo experimental data of two dissolution tests on a PWR UO_x fuel with a local burnup of 73 $MWd\cdot(kg_{HM})^{-1}$. In contrast to the studies performed by the other WP3 partners JRC-KA, KIT-INE and Studsvik, these two experiments of EURECAT were performed under oxidising conditions.

Experiments “73BIC” and “73YCWCa” were conducted each with a cladded segment of the irradiated PWR UO_x fuel exposed to a NaCl-BIC type solution and YCWCa solution, respectively. Aqueous concentrations of actinides (Am, Cm, Np, Pu and U) and of selected fission products (Cs, Mo, Rb, Sr, Tc and Zr) of the two experiments are reported in Table 10 and Table 11. In these tables, concentrations of I in experiment with YWCa solution and three measurements of Ba in the experiment with NaCl-BIC type solution are given, too. Further details about the experiments are reported by Kokinda et al. [5].

Table 10: Aqueous concentrations of actinides (Am, Cm, Np, Pu and U) and fission products (Cs, Ba, Mo, Rb, Sr, Tc and Zr) in experiment 73BIC with irradiated UOx fuel (73 MWd/kg$_{(HM)}$).

time (days)	U conctr. (mol L^{-1})	Pu conctr. (mol L^{-1})	Np conctr. (mol L^{-1})	Am conctr. (mol L^{-1})	Cm conctr. (mol L^{-1})
0.06	7.4E-07	5.8E-09	6.6E-10	4.7E-10	1.4E-10
0.17	3.3E-07	1.9E-09	3.7E-10	1.5E-10	3.0E-11
1	6.0E-07	2.0E-09	1.3E-09	1.1E-10	2.7E-11
2	8.5E-07	6.3E-09	7.1E-10	3.9E-10	8.8E-11
5	4.0E-06	2.0E-08	1.6E-09	1.9E-09	5.7E-10
9	5.0E-06	2.2E-08	9.9E-10	4.5E-09	1.4E-09
16	6.6E-06	2.9E-08	2.1E-09	8.5E-09	2.7E-09
41	1.5E-05	5.3E-08	3.2E-09	2.0E-08	6.5E-09
111	1.8E-05	5.5E-08	4.1E-09	1.6E-08	5.9E-09
210	4.5E-06	3.7E-08	4.4E-09	1.2E-08	4.8E-09

time (days)	Ba conctr. (mol L^{-1})	Gd conctr. (mol L^{-1})	Tc conctr. (mol L^{-1})	Sr conctr. (mol L^{-1})	Mo conctr. (mol L^{-1})	Zr conctr. (mol L^{-1})	Rb conctr. (mol L^{-1})	Cs conctr. (mol L^{-1})
0.06	4.9E-09	n.g.	1.8E-08	6.7E-09	1.3E-07	7.6E-09	1.7E-07	6.1E-06
0.17	4.0E-09	n.g.	8.4E-09	8.7E-09	5.7E-08	1.9E-09	1.5E-07	4.7E-06
1	2.8E-08	n.g.	7.8E-09	3.1E-08	1.0E-07	1.3E-09	2.5E-07	7.8E-06
2	7.6E-08	n.g.	5.3E-09	4.4E-08	5.5E-08	1.9E-09	3.9E-08	4.5E-06
5	3.4E-07	n.g.	4.5E-09	1.9E-07	3.9E-08	1.1E-09	7.6E-08	1.1E-05
9	1.7E-07	n.g.	3.4E-09	9.8E-08	2.3E-08	1.5E-09	8.4E-08	4.0E-06
16	1.4E-07	n.g.	4.0E-09	7.8E-08	2.8E-08	2.0E-09	6.7E-08	1.8E-06
41	1.6E-07	n.g.	1.1E-08	9.5E-08	8.7E-08	2.7E-09	7.7E-08	1.4E-06
111	1.5E-07	n.g.	5.9E-08	1.1E-07	2.4E-07	2.4E-09	8.3E-08	1.1E-06
210	2.0E-07	n.g.	1.4E-07	1.8E-07	9.7E-08	2.0E-09	1.5E-07	1.5E-06

Table 11: Aqueous concentrations of actinides (Am, Cm, Np, Pu and U) and fission products (Ba, Cs, Gd, I, Mo, Rb, Sr, Tc, Zr) in experiment 73YCWCa with irradiated UOx fuel (73 MWd/kg$_{(HM)}$).

time (days)	uranium concentration (mol L^{-1})	plutonium concentration (mol L^{-1})	neptunium concentration (mol L^{-1})	americium concentration (mol L^{-1})	curium concentration (mol L^{-1})
0.06	2.8E-06	4.5E-09	4.9E-10	3.7E-10	9.2E-11
0.23	3.2E-07	2.1E-09	2.3E-10	1.5E-10	3.8E-11
1	2.3E-07	1.3E-09	2.8E-10	7.3E-11	1.1E-11
4	2.9E-07	2.1E-09	2.5E-10	1.4E-10	3.2E-11
9	2.0E-07	8.7E-10	1.1E-10	5.0E-11	1.4E-11
16	2.4E-07	1.9E-09	1.6E-10	1.3E-10	3.5E-11
31	2.8E-07	1.2E-09	1.0E-10	7.4E-11	2.0E-11
60	4.4E-07	9.5E-10	1.0E-10	5.9E-11	1.2E-11
120	9.7E-07	2.9E-09	2.3E-10	1.9E-10	5.0E-11
240	1.8E-06	1.9E-10	2.8E-10	2.0E-10	5.0E-11
457	3.5E-06	5.3E-09	3.6E-10	2.6E-10	6.8E-11

time (days)	technetium concentration (mol L^{-1})	molybdenum concentration (mol L^{-1})	zirconium concentration (mol L^{-1})	rubidium concentration (mol L^{-1})	cesium concentration (mol L^{-1})	iodine concentration (mol L^{-1})
0.06	4.2E-08	6.7E-07	1.4E-07	1.7E-07	1.6E-05	1.0E-06
0.23	5.6E-08	8.5E-07	1.7E-08	5.6E-08	6.5E-06	3.0E-07
1	1.9E-07	2.1E-06	2.3E-09	3.2E-08	5.1E-06	1.3E-07
4	4.7E-07	5.9E-06	1.6E-09	3.3E-08	4.0E-06	3.5E-07
9	6.3E-07	7.1E-06	5.4E-10	4.9E-08	1.9E-06	8.1E-07
16	5.9E-07	6.7E-06	5.8E-10	7.3E-08	1.4E-06	1.1E-06
31	9.2E-07	8.4E-06	2.3E-10	1.6E-07	2.2E-06	1.5E-06
60	1.1E-06	8.2E-06	1.0E-10	4.3E-07	4.3E-06	8.6E-07
120	1.6E-06	1.1E-05	7.3E-11	8.4E-07	7.9E-06	1.1E-06
240	3.0E-06	1.8E-05	7.7E-11	1.2E-06	1.2E-05	1.9E-06
457	2.9E-06	2.3E-05	2.9E-11	1.6E-06	1.6E-05	4.2E-06

7 Discussion and preliminary conclusions

For comparing the results of the seven dissolution experiments, aqueous concentrations of four elements[(1)] are chosen:

- Uranium as major element of the matrix of dissolving spent UOx fuels and spent MOX fuels (Figure 1);
- plutonium as redox-sensitive element of the matrix (Figure 2);
- americium as non-redox-sensitive element of the matrix (Figure 3);
- strontium as non-redox-sensitive fission product with high solubility under the studied geochemical conditions (Figure 4).

Based on the release behaviour of uranium, plutonium and strontium, it is obvious that the experiments are characterized by a rather long initial stage of about 200 days. In this initial stage, steep gradients of concentrations versus time and fluctuations in the release behaviour are observed. In case of americium, the duration of an initial stage is not clear (Figure 3).

In the initial stage, a similar release behaviour of uranium is observed in all experiments. In the first samplings relatively high uranium concentrations were measured, followed by a decrease in uranium concentration approaching a concentration level of about $2 \cdot 10^{-8}$ mol L^{-1}. Relatively high uranium concentrations in an initial stage are interpreted as dissolution of pre-oxidized layers, followed by long-term dissolution of the UO_2 matrix. Interestingly, slightly increased uranium concentrations up to $5 \cdot 10^{-8}$ mol L^{-1} are measured in samples after 421 and 624 days (Figure 1).

Significant differences in the release behaviour of americium and plutonium amongst the experiments are observed (Figure 2 and Figure 3). Except results of experiment 73BIC, a steady strontium release is displayed in Figure 4, although the strontium release rate decreases with time.

As mentioned in chapter introduction the data of this report are preliminary and may be adjusted in continuation of the project. Accordingly, any interpretation of the data is preliminary as well. Having this in mind it is noted that in the long run of the experiments (i.e. after the initial stage of about 200 days), actinide concentrations in the two experiments with BWR fuels are considerably higher than in the experiments with PWR fuels and the lowest actinide concentrations are observed in experiment 73YCWCa, which was conducted with a PWR fuel in YWCa solution under oxic conditions. At present, a conclusive interpretation of these release behaviours cannot be provided.

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(1) Only few measurements of Xe and Kr released into the gas phase are available in four dissolution experiments with irradiated PWR MOX fuel (38 MWd/kg) and irradiated BWR UOx fuels (57 and 59 MWd/kg), whereas for the other three experiments these data are not available. Therefore data of fission gas release are no compared and interpreted in this report.

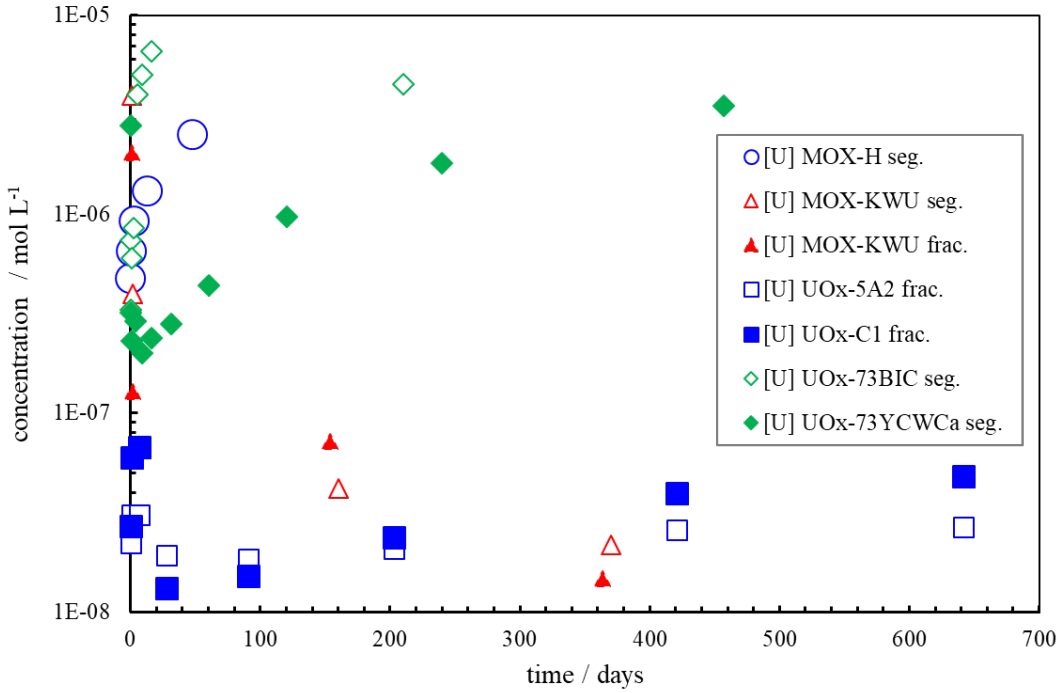

Figure 1: Concentration of uranium released into solution versus time in dissolution experiments with irradiated UOx and MOX fuels.

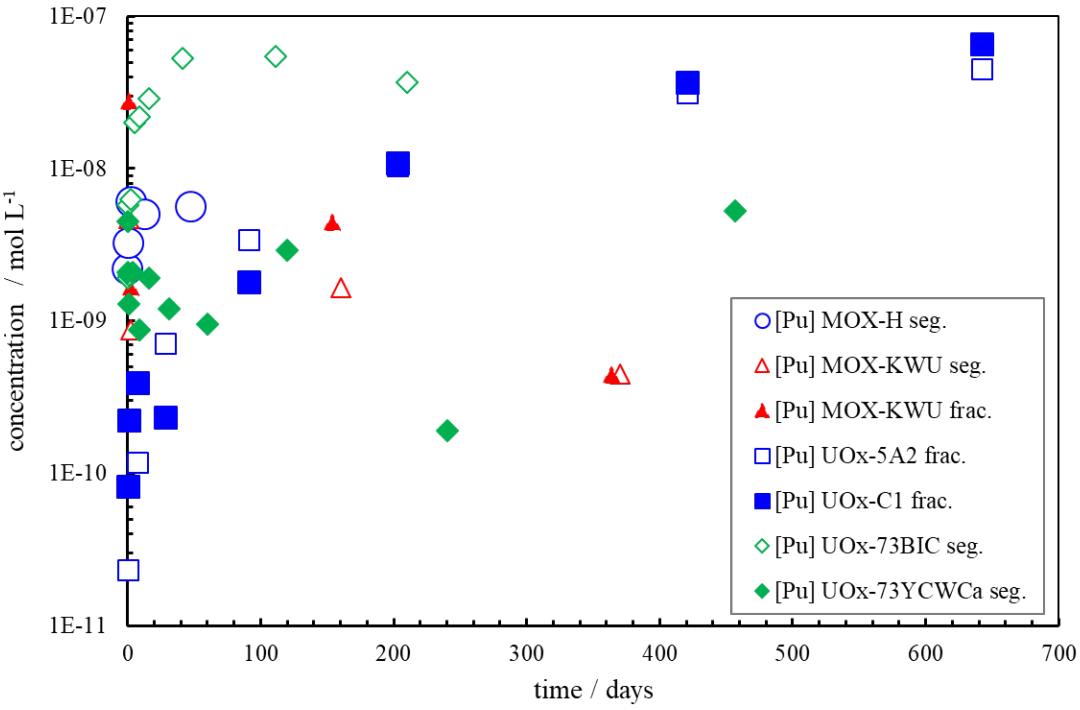

Figure 2: Concentration of plutonium released into solution versus time in dissolution experiments with irradiated UOx and MOX fuels.

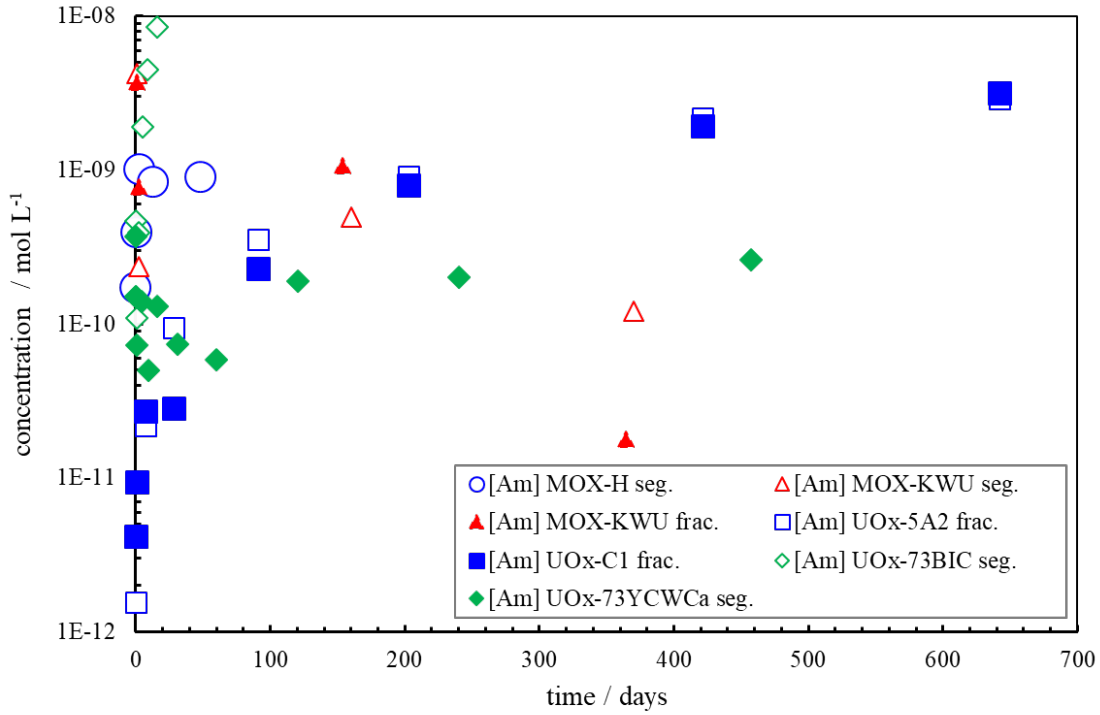

Figure 3: Concentration of americium released into solution versus time in dissolution experiments with irradiated UOx and MOX fuels.

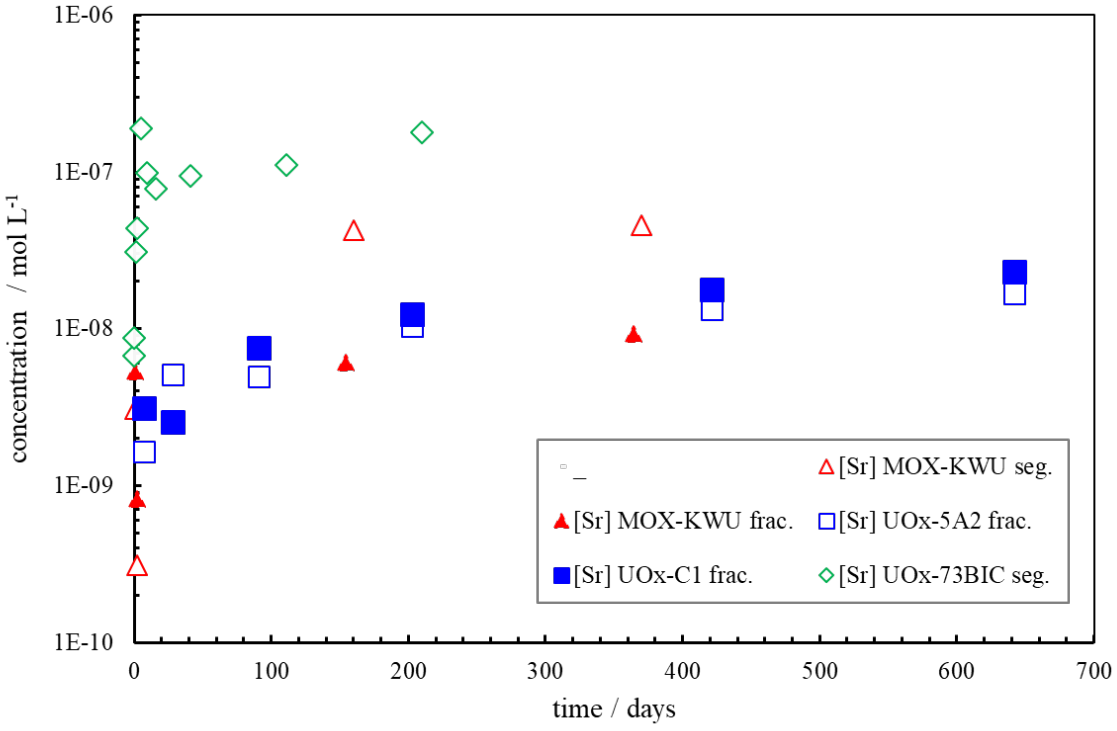

Figure 4: Concentration of strontium released into solution versus time in dissolution experiments with irradiated UOx and MOX fuels

Based on the release of five actinide elements and nine fission products into solution, dissolution of the studied spent UO_x fuel and spent MOX fuel samples is characterized by an initial stage of up to six months, characterized by relatively steep gradients in concentration versus time and relatively high uranium and plutonium concentrations. Afterwards, seem to approach steady state conditions with low release rates or to approach to solubility limits of the respective radionuclide bearing solid phases. In order to assess the dissolution behaviour of the studied irradiated nuclear fuels, which is unaffected of temporary but strong features such as dissolution of pre-oxidized layers, the radionuclide release behaviour needs to be monitored until approaching a steady state. Tentatively it is interpreted that a steady state is reached not before one year of experimental duration.

As an outlook, it is mentioned that (additional) long-term release data of the three dissolution experiments with irradiated MOX fuel samples are planned to be provided in the last year of the DisCo project.

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