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Aqueous leaching of ADOPT and standard UO_2 spent nuclear fuel under H_2 atmosphere

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ABSTRACT

Leaching results to compare the dissolution behavior of a new type of fuel with additives (Advanced Doped Pellet Technology, ADOPT) with standard UO_2 fuel are presented. Both fuels were irradiated in the same assembly of a commercial boiling water reactor to a local burnup of ~58 MWd/kgU. Fuel fragments are leached in simplified groundwater in two autoclaves under hydrogen atmosphere, representing conditions in a canister failure scenario resulting in water intrusion for a spent nuclear fuel repository. Preliminary results indicate the uranium concentration decreased to $3\text{-}4 \times 10^{-8}$ M after 421 days, slightly above the solubility of amorphous UO_2. Xe has been detected in the gas phase of both autoclaves. The concentration of Cs and I seems to gradually approach constant values, yet the redox sensitive elements continue to slowly increase with time. The preliminary data obtained supports the hypothesis that there is no major difference in leaching behavior between the two fuels.

INTRODUCTION:

New types of fuel have been developed during the last decades to improve reactor performance, reduce the fuel cycle cost and reduce the consequences in case of fuel failure. 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 [1].

From the safety perspective of a deep geological repository for spent nuclear fuel (SNF), new type of fuels must fulfill the acceptance criteria of low dissolution rate under relevant repository conditions. Property changes as a consequence of minor modifications to the UO_2 matrix might affect the leaching behavior of the fuel. For this reason, it is important to gather new data on the dissolution behavior of new types of fuel containing additives. In Roth et al. (2007) [2], the Instant Release Fraction (IRF) and matrix dissolution were investigated for both standard UO_2 and ADOPT fuels under aerated conditions. In another study, the oxidative dissolution of irradiated and unirradiated UO_2 and ADOPT was compared [3]. The results show that the doping had little to no effect on the matrix dissolution, while some differences were observed in the release of elements with low solubility in UO_2 such as Cs, Mo and Tc.

In this study, the behavior of ADOPT fuel will be compared to the performance of standard UO_2 fuel under identical conditions in the presence of hydrogen.

The main 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 behavior between the two fuels. The preliminary results for the ongoing experiment are presented.

EXPERIMENTAL DETAILS:

The experiments are being performed on fuel fragments without cladding. The selected fragments have already been leached under aerated conditions in a previous campaign (FIRST Nuclides) [2]. The fuels and their main parameters of interest are listed in Table 1. The two fuels have been irradiated in the same fuel assembly and therefore have very similar power histories.

Table 1. Fuels selected for the experiments performed at Studsvik.

Sample name	Reactor type	Fuel type	FGR [%]	Calculated BU (rod average) [MWd/kgU]
5A2	BWR	Std. UO_2	2.4	57.1
C1	BWR	ADOPT (Al/Cr doped UO_2)	1.4	59.1

As mentioned, these same fuel fragments have already been leached in a previous campaign. Thereafter the samples were stored in a hot cell for 3 years for later use. For this reason, the fuel fragments (2 g of each fuel) were exposed to an initial leaching period (washing step) under aerated conditions in 200 ml 10:10 mM NaCl:$NaHCO_3$ solutions in the Hot Cell Laboratory at Studsvik. The main objective of this initial step is to attempt to wash away any pre-oxidized phases formed during air storage in cell by exposing them to relatively high $NaHCO_3$ concentrations. Figures 1a and 1b show the collected fuel fragments and a leaching flask with the fuel immersed in the washing solution.

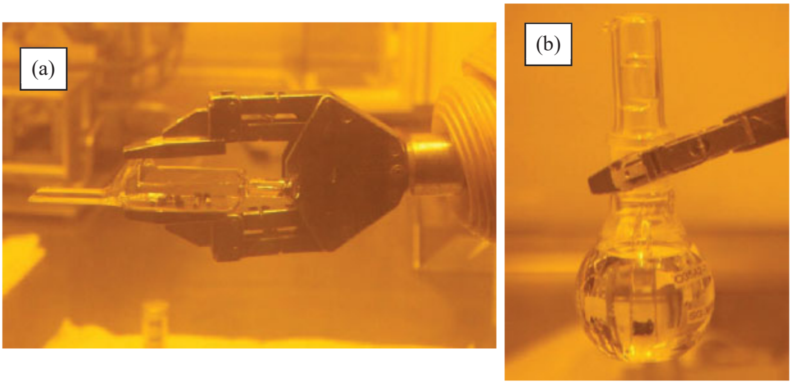

Figure 1. (a) One batch of fuel fragments and (b) flask containing fuel samples.

The washing step was divided into a total of 5 contact periods as shown in Table 2. At the end of each contact period the glass baskets containing the fuel were transferred into a new flask containing fresh washing solution.

Table 2. Contact periods for the washing step.

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

At the end of each contact period, liquid samples were taken and centrifuged for 1h at 74 000 g to try to separate colloids from the solution.

Thereafter the aqueous samples were preserved in either 1% HNO_3 (to prevent precipitation of metals and sorption losses to the container walls) or 0.5% TMAH (to prevent iodine evaporation) 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 the washing step, both fuels were placed into 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 (P4 10-16 µm pore size). The external sampling line is made of stainless steel with two valves in series. Figures 2a and 2b show the internal and external parts of the autoclaves.

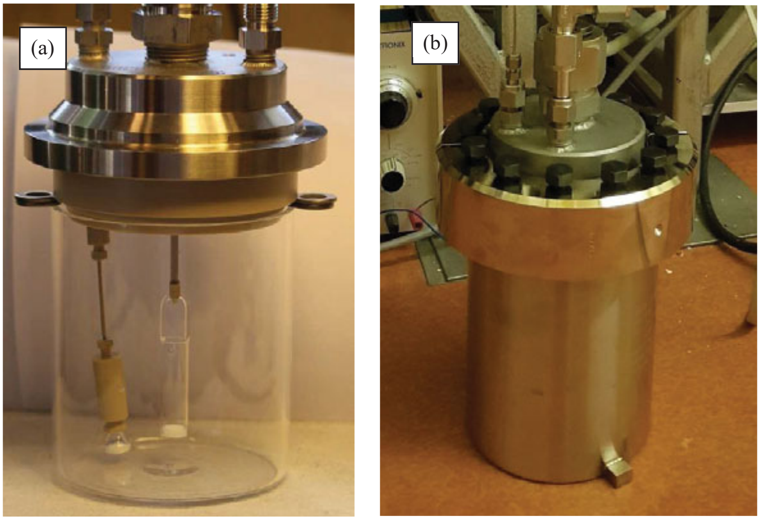

Figure 2. (a) Autoclave internals and (b) exterior of the autoclave.

The free internal volume of the autoclaves 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 glass 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 with argon for 30 min to minimize the air content. After loading the quartz baskets containing the fuel, the autoclaves were closed and sparged with argon for a further hour. 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. This is done to avoid air intrusion in the system during the re-pressurization procedure and to facilitate the gas phase composition calculations.

The concentration of radionuclides of interest in the autoclave solution will be sampled 9 times over 2 years (sampling both the liquid and gas phases). The sample solutions are analyzed in the same way as the solutions from the washing experiments. In addition, the composition of the gas phase is analyzed 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.

Table 3. Autoclave sampling points. Samples already taken and analyzed 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	421	✓	✓
8	670	April 2020	April 2020
9	730	June 2020	June 2020

Each sample point is taken in triplicate. The first sample (A) is used to rinse the sampling system and it is not analyzed (~2 ml). Samples B and C (8 ml each) are centrifuged at 74 000 g for one hour and thereafter the supernatant is removed and preserved as described above for the washing samples.

PRELIMINARY RESULTS AND DISCUSSION

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

Washing step

The uranium release rate during washing for both fuels is plotted against cumulative time in Figure 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.

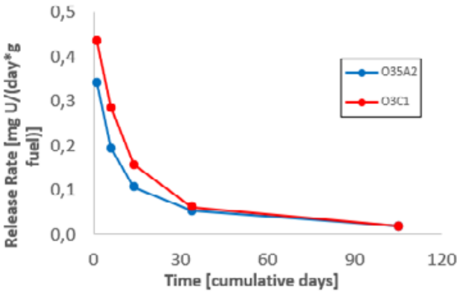

Figure 3. Uranium release rate as a function of time during the pre-wash. O35A2 corresponds to the std. UO_2 fuel and O3C1 to ADOPT.

Leaching under H_2 atmosphere

The initial pH and carbonate concentration in the leaching solution were determined to be 8.2 and 2 mM respectively.

Gas phase analysis

Table 4 and 5 summarize the evolution of the composition of the gas phase in the two autoclaves.

Table 4. Pressure and gas composition autoclave O35A2 (Std. UO_2)

O35A2	Gas	G1	G2	G3	G4	G5	G6
(Std. UO_2)	Kr [%]	<0.001	<0.001	<0.001	<0.001	<0.001	0.001
	Xe [%]	<0.001	<0.001	0.001	0.001	0.002	0.002
	H_2 [%]	98.071	97.605	97.040	97.031	96.995	96.971
	He [%]	0.113	0.522	1.015	1.029	1.058	1.065
	N_2 [%]	0.010	0.011	0.016	0.023	0.033	0.042
	O_2 [%]	0.006	0.006	0.006	0.007	0.007	0.007
	Ar [%]	1.800	1.856	1.920	1.909	1.904	1.912
Autoclave Pressure	[bar]	50.23	43.54	35.19	31.28	27.57	25.12
Duration	[days]	1	6	34	91	211	432

Table 5. Pressure and gas composition autoclave O3C1 (ADOPT)

O3C1	Gas	G1	G2	G3	G4	G5	G6
(ADOPT)	Kr [%]	<0.001	<0.001	<0.001	<0.001	<0.001	0.001
	Xe [%]	<0.001	<0.001	0.001	0.001	0.001	0.002
	H_2 [%]	98.901	98.228	98.695	97.562	97.435	97.319
	He [%]	0.056	0.274	0.724	0.847	0.934	0.977
	N_2 [%]	0.010	0.011	0.014	0.017	0.023	0.025
	O_2 [%]	0.006	0.006	0.006	0.006	0.008	0.008
	Ar [%]	1.027	1.481	1.560	1.567	1.598	1.668
Autoclave Pressure	[bar]	49.02	43.77	37.72	34.41	31.98	30.07
Duration	[days]	1	6	34	91	211	432

It must be noted that the Kr and Xe values were very close to the quantification limit making it difficult to obtain reliable values. However, from the first leaching month, the isotopic composition of Xe in the gas phase matches the Xe inventory in the fuel fairly well. This was not the case for Kr, where the levels detected were clearly below quantification limit. This implies nonetheless that fission gas has been released from both samples to some extent. The oxygen concentration in the system remains constant at low levels. No significant air intrusion/leakage in the system (assessed by the N_2 concentration) is observed.

Aqueous phase analysis

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

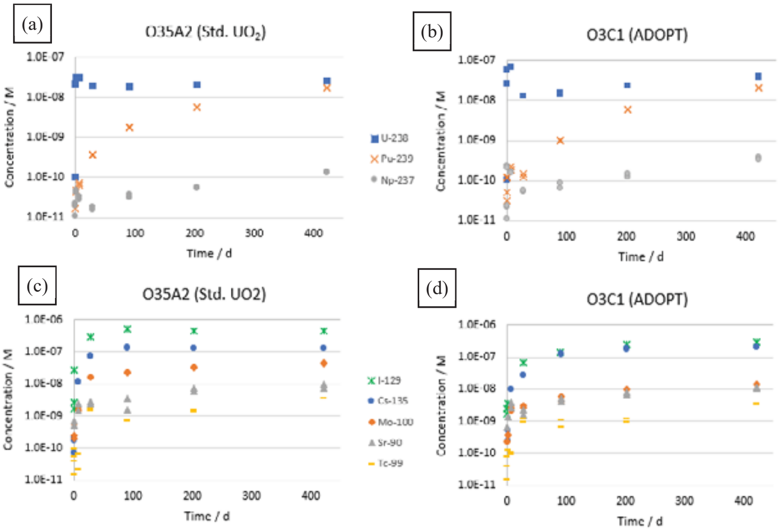

Figure 4. Autoclave concentrations of U-238, Pu-239 and Np-237 (a,b) and I-129, Cs-135, Mo-100, Sr-90 and Tc-99 (c,d). The plots to the left belong to autoclave O35A2 (standard UO_2) and to the right to autoclave O3C1 (ADOPT).

As can be seen in Figure 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. However, this effect seems to vanish with time. For both autoclaves, the U-238 concentration increases at a very slow rate reaching a concentration of 3-4x10^{-8} M after 421 days, one order of magnitude higher than the solubility for amorphous UO_2 (2-5x10^{-9} M) [4]. The Pu concentrations are also unexpectedly high at ~2x10^{-8} M, while relative low concentrations for Np are observed in both cases (~ 2x10^{-10} M), although one to two orders of magnitude higher than values reported by a previous study on high burnup standard UO_2 fuel under hydrogen conditions [5].

Highly soluble nuclides such as I-129 and Cs-135 increased steadily during the first month reaching a constant level for the standard UO_2 fuel. The ADOPT sample is also rapidly transitioning to near-constant concentrations; however, a moderately increasing trend is still observed. The major release of other elements of interest such as Mo-100, Sr-90 and Tc-99 occurs within a few days, yet their concentrations continue to increase slowly with time in both autoclaves.

The largest difference between both fuels can be observed in the leaching behavior of I-129. The FIAP of an element (Fraction of Inventory in Aqueous Phase) is calculated by dividing the mass of the element present in the aqueous phase by the mass of the element in the spent nuclear fuel [6]. After 1 year and 2 months, the FIAP for I-129 for the standard UO_2 fuel is 7.0 %, while for ADOPT is 4.6 %, without taking into account the fraction already removed from the previous leaching [2]. This difference can be explained given the larger grain size in ADOPT fuel, reducing the release of volatile elements such as I-129 during reactor operation. Furthermore, it is interesting to note that the released I-129 fraction is higher than the FGR for both fuels (see Table 1).

At this point in the experiment, radionuclide concentrations remain fairly low but considerably higher than when compared to previous leaching studies under hydrogen atmosphere [5, 7-9]. Surprisingly high relative concentrations of Pu are found in both autoclaves, still continuously increasing as of the most recent sampling point of 432 days. Another interesting observation is that other sensitive redox elements such as Tc-99 and Mo-100 are not only one order of magnitude higher than expected but also steadily increasing with time. This behavior is atypical in a system where reducing conditions are expected.

We hypothesize that this anomalous behavior could be explained by the nature of the fuel samples that were selected. As indicated in the experimental section, the fuel samples that are being leached had previously been corroded for 3 years under aerated conditions and later stored in a hot cell; they were then again exposed to aerated conditions during the washing phase of this study. As a consequence, the fuel surface is oxidized, grain boundaries are opened, and the exposed reactive surface area is increased. This is in line with the data reported by Gray [10], where after 169 days of oxidative flow-through dissolution in a solution containing 0.2 mM carbonate the surface area of the fuel fragments increased by a factor of five. In addition to this increased surface area, pre-oxidized phases were presumably formed during humid storage in a hot cell.

If the pre-oxidized layers in our samples were not completely removed from the fragments' surface, these pre-oxidized layers could interfere with the catalytic effect of H_2, thereby explaining the increasing concentrations of redox sensitive elements. Similar observations were found by Puranen [11] in a study where high burnup fuel was leached under H_2 atmosphere. This "erratic" behavior (similar to that seen in this study) was attributed to the extended air milling for sample preparation, which created unusually large amount of pre-oxidized phases and a higher surface area. To support this hypothesis, another experiment was performed by the authors with freshly cut fuel that was used after a short pre-wash. In this experiment, the concentrations for all radionuclides of interest were considerably lower, in line with the expected results under H_2 conditions.

Regardless of the atypical higher concentrations of some radionuclides in both autoclaves, the overall doping effect on the leaching behavior seem to be small. The preliminary results presented so far support the hypothesis that there is no major difference in leaching behavior between the two fuels. To further support this hypothesis, 2 additional sampling points (both liquid and gas) are planned in the next year as summarized in Table 3. The final conclusions will be drawn once all the leaching data is available.

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