



Aqueous leaching of Cr₂O₃-doped UO₂ spent nuclear fuel under oxidizing conditions

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Abstract

Understanding the leaching behavior of spent nuclear fuel is crucial for the safety assessment of deep geological repositories to dispose spent nuclear fuel. During the last decades, new types of nuclear fuel are being introduced in commercial reactors. These new fuels with additives such as chromium oxide (Cr₂O₃) have an impact on the UO₂ microstructure and therefore might affect properties relevant to the safety assessment. The main goal of this investigation is to understand the effects of Cr-doping on the instant release fraction of fission products. A sample consisting of fuel fragments and separated cladding was leached in simplified groundwater under aerated conditions at Studsvik's Hot Cell Laboratory. Data from leaching experiments performed on Cr-doped fuel manufactured by Framatome are presented and compared to other commercial Cr-doped fuel manufactured by Westinghouse (Advanced DOPed Pellet Technology, ADOPT) and standard UO₂ fuel.

Introduction

Programs for deep geological repositories are being developed in several countries around the world to safely dispose of spent nuclear fuel. Therefore, understanding the behavior of spent nuclear fuel under relevant conditions is crucial for the safety assessment of these facilities. The behavior of UO₂ based spent nuclear fuel has been extensively studied and it is nowadays considered reasonably well known. However, during the last decades new types of nuclear fuel are being introduced in commercial reactors to improve reactor performance. Two examples of these fuels are the ADOPT fuel (Advanced Doped Pellet Technology, developed by Westinghouse) and Cr-doped fuel (developed by Framatome, from now on referred to as “Cr-doped F”). These new types of modern fuels contain additives such as chromium oxide (Cr₂O₃) which have an impact on the UO₂ microstructure and therefore might affect properties relevant to the safety assessment. Available data report that both Cr-doped F and ADOPT fuel have 5 times larger grain size compared to standard UO₂ [1–3]. Chromia doped fuels have been shown

to reduce Fission Gas Release (FGR) [2], improve behavior during power transients and diminish potential for fuel washout from a failed fuel rod [3]. The changes in properties may affect fuel behavior in the spent fuel repository, and therefore, dissolution data are required to ensure the safety assessment also covers these modern fuel types.

Nilsson et al. and Barreiro-Fidalgo et al. studied the behavior of ADOPT fuel under aerated conditions and in presence of H₂ overpressure and compared it to the performance of standard UO₂ [4–7]. These studies showed that the Cr-doping had little to no effect on fuel dissolution behavior under both oxidizing conditions and in the presence of hydrogen. Nevertheless, a lower release of iodine and cesium (elements associated to the Instant Release Fraction, IRF) was observed for the doped samples.

As doping levels differ between different doped fuel types, it is of interest to compare the results obtained for the ADOPT fuel with doped fuel from other manufacturers. In this study, we have investigated the instant release behavior of Cr-doped fuel and compared it to ADOPT and standard UO₂ fuel.

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Experimental

The selected fuel sample for the leaching experiments, together with the fuels used for comparison [6] are listed in Table 1.

Table 1 Fuel selected for the current leaching experiment (Cr-doped F sample), compared with ADOPT and standard UO₂

Fuel sample	Cr-doped F (this experiment)	ADOPT	Std. UO ₂
Irradiation time	2009–2014	2000–2008	2000–2008
Reactor	Ringhals 4	Oskarshamn 3	Oskarshamn 3
Fuel type	Cr-doped UO ₂	Cr-doped UO ₂	UO ₂
Initial enrichment [%]	3.9	4.1	3.5
Local BU [MWd/kgU]	59	65	63
Fission gas release [%]	1.8	1.4	2.5

The F in “Cr-doped F” stands for Framatome, to avoid confusion with the Cr-doped sample manufactured by Westinghouse, ADOPT

Out of the 3 fuel specimens listed in Table 1, only the “Cr-doped F” sample was leached in this study. The fuel sample was leached as fuel fragments and separate cladding under aerated conditions in simplified groundwater at hot cell temperature (20 °C ± 2).

Available preexisting leaching data up to 3 months from the specimens ADOPT and standard UO₂ can be found in [6]. The FGR has been measured experimentally at Studsvik Hot Cell Lab for all three specimens.

Sample preparation

A gamma scan of the fuel rod was examined prior the leaching experiment to identify a suitable sample for the experiment. This sample was selected from a flat profile and close to a target burnup of 60 MWd/kgU. Thereafter the sample was cut at mid-pellet positions consisting of approximately 2 fuel pellets (1 whole pellet and 2 adjacent halves).

The fuel fragments were separated from the cladding by crushing the sample. This method was chosen to avoid potential losses of iodine attributed in a previous study to axial cutting of the sample [6]. After successfully detaching the fuel from the cladding, it was clearly observed that a large fraction of small fragments and powder was produced by this method. The fuel fragments and powder and the cladding were weighed separately before starting the leaching experiments. The weight of the sample inside the flask was 12.55 g and 3.11 g, respectively.

Leaching of Cr-doped F sample

The fuel sample together with the cladding was introduced in a glass basket with a P2 filter in the bottom (pore size 40–100 µm). Thereafter the basket was introduced in a glass flask containing 200 ml of simplified groundwater

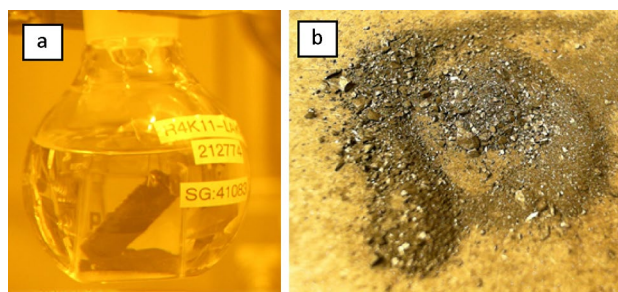


Fig. 1 **a** Picture of a leaching flask containing 200 ml of leaching solution. The fuel and cladding sample were located inside a glass basket with a P2 filter in the bottom. **b** Close-up image of the fuel fragments and powder leached. The size of the biggest fragments were ~3–4 mm while the largest fraction of the sample was fragments/powder well below 1 mm

(10:2 mM NaCl:NaHCO₃) (Fig. 1a). The leaching experiment was divided into 6 contact periods with a total cumulative leaching time of 331 days. At the end of each contact period the basket containing the sample was transferred into a new flask containing fresh leaching solution. Liquid samples were taken at the end of each contact period for analysis by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for masses 82–254 and I-129, gamma spectrometry for Cs-137 as well as pH and carbonate measurement. The experimental uncertainty of the data obtained is estimated to be 5–10%. Prior analysis the samples were centrifuged for 1 h at 74,000×g to separate colloids or small particles from the solution except for the pH and carbonate sample.

Results

The measured pH and carbonate concentrations after each of the 6 contact periods are presented in Table 2.

The release of radionuclides of interest during the leaching experiment are shown in Figure 2 as cumulative Fraction of Inventory in the Aqueous Phase (FIAP). The FIAP for a given contact period is calculated according to Eq. 1:

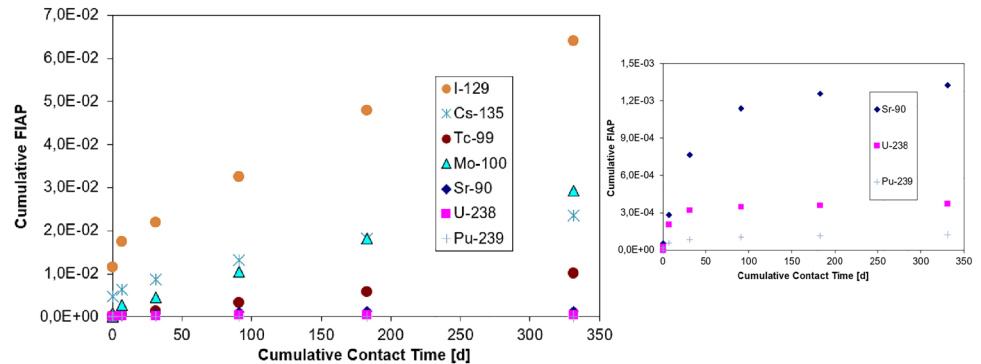
$$\text{FIAP}_i = \frac{m_{i,\text{aq}}}{m_{i,\text{SNF}}} = \frac{c_i \cdot V_{\text{aq}}}{m_{\text{SNF}} \cdot H_i} \quad (1)$$

where $m_{i,\text{aq}}$ is the mass of the element i in the aqueous phase in g, $m_{i,\text{SNF}}$ the mass of the element i in the spent nuclear fuel sample, H_i is the fraction of inventory for the nuclide i in g/g, c_i is the concentration of element i in solution in g/L, V_{aq} is the volume of solution in L.

As can be seen, elements susceptible to rapid release upon contact with water such as I-129 and Cs-135 showed the initial highest release. As the experiment progressed it was clear that I-129, Cs-135, Mo-100 and to a lower extent

Table 2 Carbonate concentration and pH of leaching solutions at each sampling point

Contact period	Initial	1	2	3	4	5	6
Contact period length (day)	0	0.1	7	24	60	92	148
pH	8.2	8.2	8.1	8.0	8.1	7.9	7.9
[HCO ₃ ⁻] (mM)	2.4	2.4	2.5	2.2	2.1	1.9	1.8

Fig. 2 Cumulative release fractions of selected radionuclides of interest during the Cr-doped F leaching experiment as a function of cumulative leaching time. A zoom in the lowest cumulative FIAP range is presented for the isotopes Sr-90, U-238 and Pu-239. The uncertainty associated to the results is estimated to be 5–10%**Table 3** Summary of the cumulative FIAP of selected radionuclides after 6 months of leaching under aerated conditions

	Cr-doped F	ADOPT	Std UO ₂
Cumulative time [d]	183	181	181
I-129	4.8×10^{-2}	3.1×10^{-2}	3.7×10^{-2}
Cs-135	1.9×10^{-2}	8.7×10^{-3}	1.1×10^{-2}
Mo-100	1.8×10^{-2}	1.0×10^{-2}	5.8×10^{-3}
Tc-99	5.9×10^{-3}	4.8×10^{-3}	3.7×10^{-3}
Sr-90	1.3×10^{-3}	1.2×10^{-3}	9.3×10^{-4}
Pu-239	1.2×10^{-4}	4.0×10^{-5}	2.2×10^{-5}
U-238	3.6×10^{-4}	3.2×10^{-4}	3.5×10^{-4}

Preexisting leaching data up to 3 months for ADOPT and Std. UO₂ can be found in [6]. The datapoint corresponding to a cumulative FIAP of 6 months is reported in this study

Tc-99 showed a significant higher release than Sr-90, U-238 and Pu-239. The general leaching behavior of this sample was in line with similar leaching studies under aerated conditions reported in the literature [4, 6–8].

Although the trends for the different radionuclides were like those found in ADOPT and standard UO₂, a few differences were observed. Table 3 shows the cumulative FIAP of selected radionuclides. Note that a cumulative leaching time of 6 months is taken as reference due to the lack of a 1-year leaching datapoint for ADOPT and std UO₂.

It can be seen in Table 3 that the release of elements associated to the IRF (I-129 and Cs-135) was slightly lower for the ADOPT specimen compared to standard UO₂. This was consistent with the difference in the measured FGR between the two fuels (1.4% and 2.5%, respectively) and it was attributed the larger grains present in chromia-doped samples [1–3]. In previous studies, many authors have

correlated the IRF with the FGR [9]. Given that the FGR of the Cr-doped F sample (1.8%) was lower than the standard UO₂ fuel but higher than ADOPT, a similar correlation for I-129 and Cs-135 could be expected. This is however not the case as the Cr-doped F sample released more iodine and cesium than the other two fuel specimens. This observation is discussed further below. Elements segregated from the UO₂ matrix such as Mo and Tc showed a higher release in both doped samples compared to the undoped fuel.

It is worth noting that all cumulative FIAPs for the Cr-doped F sample are higher than both ADOPT and standard UO₂. This was not expected since Cr-doped F fuel can be considered analogous to ADOPT in several aspects such as lower FGR and larger grain sizes compared to standard UO₂. This behavior can be attributed to differences in fragment size between the 3 fuel samples. Even though the same sample preparation method was used for all 3 samples, it was observed that a significant higher fraction of small particles and powder were created during the Cr-doped F sample preparation compared to the other two fuels. A potential explanation could be the use of higher forces during this study while crushing the sample. It should be emphasized that no sieving or measurement of fragment sizes have been performed to confirm this hypothesis. The smaller the fragment size, the larger the surface area exposed to the leaching solution which leads to faster dissolution and radionuclide release. These differences in dissolution rates become obvious when the leaching behavior of larger fragments obtained by axial cutting were compared to crushed samples [6].

It is therefore rather difficult to compare between samples with different fragment sizes and consequently different exposed surface areas. To partially overcome these differences the cumulative FIAP of each sample were normalized

Table 4 Cumulative FIAPs normalized to U-238 after 6 months of leaching under aerated conditions

	Cr-doped F	ADOPT	Std UO ₂
Cumulative time [day]	183	181	181
I-129	133.3	103.2	104.5
Cs-135	50.1	44.0	51.9
Mo-100	50.4	33.3	16.5
Tc-99	16.3	15.9	10.5
Sr-90	3.5	4.1	2.7
Pu-239	0.3	0.1	0.1
U-238	1	1	1

to their respective cumulative U-238 FIAP. This way, any excess of radionuclide release due to higher matrix dissolution rates should be corrected. It is however important to note that not all parameters are canceled using this normalization. Other factors like exposed grain boundaries, cracks and pores can affect to what extent each radionuclide is released. The normalized cumulative FIAP after 6 months of leaching is shown in Table 4.

When normalizing FIAPs the differences between samples decrease, to the point that I-129 release is rather similar between ADOPT and std.UO₂. However, the Cr-doped F sample shows a higher I-129 release. With regard to Cs release, any difference observed is within the experimental uncertainty estimated to 5–10%. The release of Mo-100 seems to be clearly higher in the Cr-doped samples compared to standard fuel. A potential explanation for the high iodine release may be that iodine, behaving much like fission gases in the fuel during irradiation, is segregated to intragranular pores exposed due to the small fragment size of the sample.

No conclusions on the matrix dissolution behavior of the samples can be drawn given the relative short leaching time of these experiments.

Summary

In this study, a chromia-doped spent nuclear fuel sample (developed by Framatome) was leached under oxidizing conditions and compared its performance to similar studies with another chromia-doped fuel (ADOPT) and standard UO₂. The results have shown that:

- Radionuclide concentrations for the Cr-doped F sample were within the expected range when compared to similar leaching studies.

- Higher cumulative FIAP of all radionuclides were found in the Cr-doped sample compared to ADOPT and standard UO₂. These differences decreased for most radionuclides when the FIAPs of the radionuclides were normalized to the U-238 FIAP. This could indicate that a hypothetical higher surface area in the Cr-doped F sample and not the Cr-doping could be responsible for the higher radionuclide release.
- The release of iodine is significantly higher than the FGR. This appears not to be related to matrix dissolution, however, may be related to the exposure of intragranular pores.

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Data availability The raw/processed data required to reproduce these findings cannot be shared at this time due to technical and time limitations and the data also forms part of an ongoing study.

Declarations

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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