Leaching of spent nuclear fuels in aerated conditions: Influences of sample preparation on radionuclide release patterns

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ABSTRACT

The release of radionuclides from spent nuclear fuel upon contact with water is a central issue for the assessment of the safety of geological disposal concepts. Several studies have been conducted aiming at understanding matrix dissolution as well as the rapid/instant release of radionuclides separated from the UO_2 matrix; there are however questions remaining regarding how higher burn-up affects the amount of fission products segregated to the fuel-cladding gap and grain boundaries.

In this study we have performed aerated fuel corrosion and leaching experiments using spent nuclear fuels with a range of burnups, from ~52 to ~70 MWd/KgU. The samples have been prepared in different manners in order to investigate the release of the segregated fission products from the gap and the grain boundaries. Thus, the fuel samples are prepared either as segments with the cladding attached, as fragments without cladding, or as milled powder. The fuel samples are leached in aqueous solution in aerated conditions and the radionuclide release is monitored during several contact periods for up to five years total leaching time.

The results from the leaching of fuel segments reveal congruent release of e.g. europium and neodymium whereas the release of those elements was lower than the U-238 release for the fragment samples. Potential explanations for this are discussed in the paper.

The results show that the release rates of elements segregated from the fuel matrix were in general found to be lower from segments samples as compared to fragment samples, which can be attributed to the closed fuel-cladding gap inhibiting the exposure of the gap inventory to water for the high burnup fuels used in this study.

Leaching of fuel powder (78 MWd/kgU local BU) by simultaneous grinding and leaching showed a fractional release of Cs-137 and I-129 of 1.5% and 1.8% respectively.

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1. Introduction

The rate at which spent nuclear fuels release their radionuclide content upon water contact is a central issue to the safety assessment of spent nuclear fuel repositories. The majority of the radionuclides in spent nuclear fuels are distributed within the UO_2 matrix of the fuel [1] and their release will be governed by the matrix dissolution [2]. A fraction of the fission products is however segregated from the fuel matrix and will be leached from the gap between the fuel and the cladding, from the UO_2 grain boundaries or from separate phases within the fuel.

Under the reducing conditions expected in a future deep repository, the solubility of UO_2 is very low. However, the formation of oxidants by radiolysis of water may alter these conditions and lead to oxidative dissolution of the UO_2 matrix. In this study the experiments are performed under aerated conditions, which can be considered quite penalizing.

Even under air, the matrix dissolution is a relatively slow process, whereas the release of segregated elements from the gap and grain boundaries is faster and is often referred to as the "Instant Release Fraction" (IRF). The chemical state and the distribution of each radionuclide in the fuel will therefore highly influence its release rate. The chemical composition and microstructure of irradiated nuclear fuel have been studied extensively [1–5] and the elements are not homogeneously distributed with in the fuel pellets. This is due to proximity to the moderator (usually water):

neutrons close to the pellet periphery have lower kinetic energy, and therefore cause a higher number of fissions. As a consequence, the radial burnup across a spent fuel pellet is not uniform but increases significantly towards the periphery. This also applies to plutonium build-up by neutron capture in U-238 followed by fission of the formed plutonium. For these reasons the content of fission products and of minor actinides is higher near the pellets outer radius [6]. Furthermore, thermal gradients during reactor operation can affect the grain size and cause fracturing of the fuel as well as migration of volatile elements such as Cs and I to grain boundaries, fractures and the gap between the fuel and the cladding [5].

Ewing [5] divides the elements into five categories: (1) finely dispersed bubbles in the fuel grains containing fission product gases, such as Xe, I and Kr; (2) metallic precipitates (ε-particles) containing metallic fission products, such as Mo, Tc, Ru, Rh and Pd; (3) oxide precipitates of Rb, Cs, Ba and Zr; (4) elements forming solid solutions with the UO_2 matrix e.g. Sr, Zr, Nb and lanthanides and (5) transuranium elements that substitute for U in the UO_2.

In this study we investigate the effect of sample preparation on the radionuclide release patterns of spent nuclear fuels. As mentioned above, spent nuclear fuel is a highly heterogeneous material and different sample preparation methods (cutting, milling etc.) resulting in different sample types (fuel segments with cladding, fuel fragments or milled fuel fragments) will allow for water access to different fuel compartments (e.g. gap and rim zone, grain boundaries) the leaching behavior is expected to be influenced.

The difference in local burnup at the periphery and in the pellet center increases disproportionately with burnup. At local burnup above ~50 MWd/kgU (depending on fuel temperature) a high burnup structure (HBS) or rim structure in the outer region of the fuel is formed. This region is characterized by a transformed microstructure, consisting of small grains of submicron size and a high concentration of pores of typical diameter $1-2\,\mu m$ [6,7]. At a local burnup of 60 MWd/kgU, the HBS rim will be approximately $100\,\mu m$ thick (Fig. 5 in Ref. [6]).

When the fuel is discharged from the reactor and cools down, a gap may be formed between the pellet and the cladding due to their different thermal expansion coefficients, if the burnup is low to moderate. This gap allows for water to access the pellet surface easier than the bulk of the pellet in leaching experiments [6]. At higher burn-ups (>40 MWd/kg U) the gap typically is closed [8] and this prevents water from readily accessing the rim-region unless the cladding is removed or is damaged.

Previous studies have explored the correlation between the instant release fraction (or combined gap and grain boundary inventory) and the fission gas release (FGR) of the fuel [9-11]. The correlation is attributed to the fact that under reactor operation temperatures, volatile and segregated fission products are in a gaseous state which enhances the rate of diffusion to the grain boundaries and the fuel/cladding gap. At reactor operation temperatures, the diffusion rate of iodine is expected to be similar to the diffusion of xenon, whereas the diffusion rate of cesium is expected to be correlated to the xenon diffusion rate by a factor of $\sqrt{1/3}$, based on their different diffusion coefficients [11]. It should however be pointed out that the respective diffusion coefficients have a strong temperature dependence, potentially leading to large difference in local diffusion rates [12].

As the diffusion of fission products in the fuel matrix depends on the fuel temperature which, in turn is related to the linear power rating (LPR) it is reasonable to assume that there could be a correlation also between the IRF and the LPR, although this reasoning is somewhat simplified as it does not reflect that pins of different diameters will have different radial temperature profiles for the same LPR value.

Lemmens et al. [13] have explored the correlation between IRF and LPR and found that the data correlates for LPRs over 200 W cm-1. There also are several experimental series [10,11] relating the IRF to the FGR where the experimental data show that the release of iodine seems to reach a steady state around the FGR and the release of Cs approaches a steady state around $\sqrt{1/3}$ of the FGR, in line with the hypothesis above.

However, there are also data contradicting this hypothesis, where the release of iodine and Cs is larger than the FGR and $\sqrt{1/3}$ FGR respectively, especially for fuels with low burnup and low FGR, while lower release values than FGR or $\sqrt{1/3}$ FGR are reported for high FGR fuels [11]. A complicating factor is that the FGR and LPR values used often are rod average values and not specific to the location of the sample used in the leaching experiment, which can give misleading results as the LPR (and thus the fuel temperature and FGR) can vary significantly along the length of a fuel rod during operation.

Although the issue of radionuclide release from spent nuclear fuel under deep repository conditions has been studied for several decades [5,14,15] and much has been learned there is still a dearth of experimental data and questions remain regarding how higher burn-up affects the amount of fission products segregated to the fuel-cladding gap and grain boundaries, and at what rate these radionuclides are released upon water contact.

Therefore, we have in this study leached spent nuclear fuels with a range of burnups, from ca 52 to 70 MWd/KgU, for an extended period of time in aerated conditions in the Studsvik Hot Cell laboratory, Sweden. The samples have been prepared in different manners in order to investigate the release of the segregated fission products from the gap and the grain boundaries. Thus, the fuel samples are prepared either as segments with the cladding still attached, as fragments without cladding, or as milled powder. The fuel samples are leached in aqueous solution and the radionuclide release is monitored during several contact periods for up to five years total leaching time.

2. Experimental details

Four fuel rods with different burnup were used in this study. All fuel rods were operated in Pressurised Water Reactors (PWR). Samples covered a local burnup range from 58 to 78 MWd/kgU. Table 1 gives a summary of the operating history; further information is listed in Ref. [7].

The leaching experiments were performed under oxidising conditions at ambient temperature. For the segment and fragment leaching Allard water (synthetic groundwater) was used, for the powder leaching a solution of 10 mM NaCl and 2 mM HCO_3^- (simplified synthetic groundwater, also referred to as 10:2 solution) was used. The composition of the Allard groundwater is presented in Table 2.

The fuel segments were prepared by cutting a 20 mm piece from each rod. An initial washing step was performed (exposure to 10 mM NaCl/2 mM HCO_3^- for about 2 h) in order to remove pre-oxidized phases after which the fuel segment was immersed in 200 mL leaching solution. The leaching was performed in 10 contact periods (including the initial washing step) corresponding to a total leaching time of 1889 days (~5 years).

The fuel fragments were also prepared by cutting a 20 mm piece from each rod and an initial washing step was performed (~2 h, 10 mM NaCl/2 mM HCO_3^-) on this segment. After the initial washing, the cladding was longitudinally sawed on opposite sides of the segment in order to remove the cladding and obtain the fuel fragments. After de-cladding the resulting all fuel fragments and the cladding halves were placed in glass baskets with glass filter

Table 1
Fuel rod data.

Sample designation (Studsvik)	4I8-Q12	SUT3	3V5-Q13	AM2-K12
Reactor	Ringhals 3	Ringhals 4	Ringhals 3	North Anna 1/2
Irradiation period	1989−1994	1998−2003	2000−2005	1987−2001
Rod average BU (calculated) [MWd/kgU]	52.2	62.8	60.0	70.2
Local BU at sample position (gamma scan) [MWd/kgU]	57.9	65	62.7	78
Rod Average Linear Power Rating [kW/m]	18.3	18.1	18.3	18.6
Exp. det. FGR (Kr release) [%]	0.9	2.3	2.6	5.0
Segment leaching	X	X	X	X
Fragment leaching	X	X	X	X
Powder leaching				X

Table 2
Composition of Allard groundwater.

Element	Concentration [mM]
Ca	0.4477
Mg	0.1774
K	0.1000
Na	2.836
Silicate	0.2056
Bicarbonate	2.014
Sulfate	0.1000
Chloride	1.973
Fluoride	0.2023
Phosphate	0.001

bottom and immersed in 200 mL leaching solution. The leaching was performed in 8 contact periods (including the initial washing step) corresponding to a total leaching time of 1149 days (~3 years).

The fuel weight was around 9 g in the segment and fragment leaching experiments. All results are evaluated based on the fuel weight, no attempt to estimate the exposed surface area have been made.

After every contact period the fuel sample (segments or fragments), was transferred to a new vessel with fresh leaching solution. The used leaching solution was sampled for gamma spectrometric and ICP-MS analyses. For the fragment leaching, the solution used in the initial washing step was also sampled for ICP-MS analyses. This was however not performed for the initial washing step during the segment leaching. To compensate for this, the data from the initial washing step form the fragment leaching (the pre-leaching was performed prior to the cutting of the cladding i.e. when the fuel was is the form of a segment) has been used also in the segment leaching series. Since the fuel samples are obtained from the same rods and of similar shape and size it is reasonable to assume that the initial washing should lead to similar radionuclide release.

pH and carbonate determination were performed for the six first contact periods for the segment leaching, leading to results of pH 8.0 to 8.5 and carbonate concentrations of 98−132 ppm [7].

The influence of sorption of radionuclides on the vessel walls was evaluated by stripping of the used flasks and the centrifuge tubes for the first six contact period of the leaching of fuel segments. The stripping was performed by exposing the used flasks and the centrifuge tubes to 2 M HNO_3 for a few days (200 mL and 10 mL, respectively). The strip solutions were analysed in the same way as the centrifuged samples.

After the fragment leaching, leached AM2K12 fuel fragments were chosen for powder leaching. Two batches of ~1.8 g each were selected. One batch was transferred to a milling bowl containing 30 mL of 10:2 solution. The sample was simultaneously ground and leached for 2 min at 400 rpm. After the milling, an additional 20 mL 10:2 solution was added to the bowl and the sample was left for 30 min.

After 30 min of static leaching in the milling bowl, 4 liquid samples were taken from the bowl with a pipette. The samples
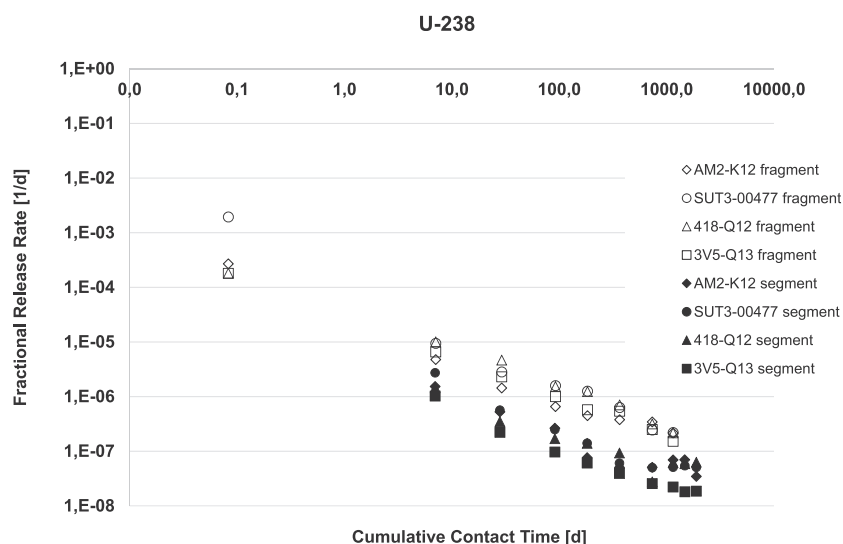
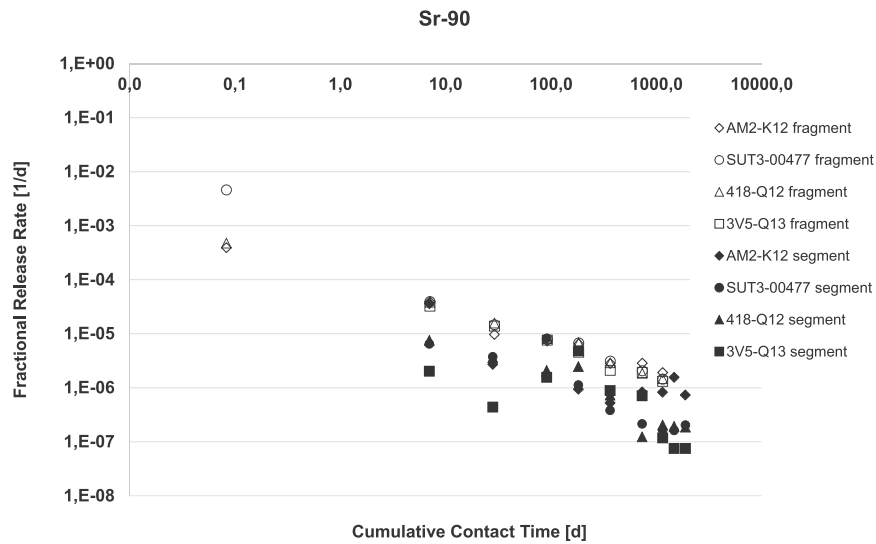**Fig. 1.** Fractional release rate of U-238 as a function of cumulative contact time.

Fig. 2. Fractional release rate of Sr-90 as a function of cumulative contact time.
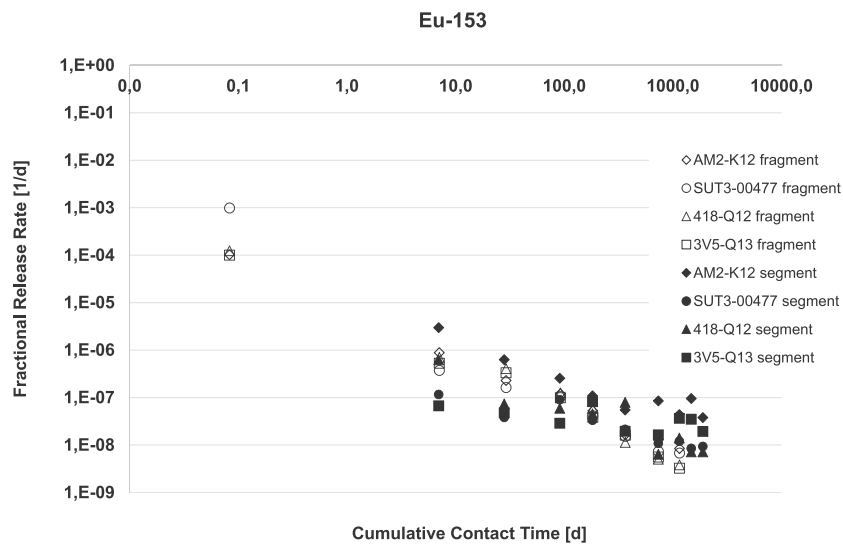

Fig. 3. Fractional release rate of Eu-153 as a function of cumulative contact time.

were immediately centrifuged, and the supernatant was removed and preserved for ICP-MS analysis. In addition, the slurry from the bottom of the bowl was sampled. This sample was centrifuged, and the centrifuge sediment was dried and prepared for SEM analysis to determine the obtained particle size distribution.

The powder leaching experiment was performed in a Fritsch Pulverisette 6 planetary ball mill. The ball mill is equipped with a tungsten carbide milling bowl and balls.

The second batch of leached AM2K12 fuel fragments (~1.8 g) were used in a parallel leaching experiment without grinding. This was done to assess the leaching from the fragment surface (as opposed to grain boundaries) caused by any potential pre-oxidation of the fuel fragments during the time between the end of the fragment leaching and the beginning of the powder leaching. The fragments were placed in 50 mL leaching solution in a bottle in

Hot Cell. After 30 min 4 samples were taken for ICP-MS analysis.

The concentration of fission products and actinides was measured with ICP-MS. All samples contained 1% HNO_3, with 1 ppb In-115 and 1 ppb Bi-209 as internal standards. Measurements in the mass range 80—254 amu were carried out. Sensitivity factors for the different elements relative to the internal standards were calculated using multi-element standards. Iodine concentrations were measured in separate samples stabilized by adding Tetra Methyl Ammonium Hydroxide (TMAH) to a concentration of 0.5%. Potential interference by Xe-129 is eliminated by using a Dynamic Reaction Cell with oxygen. Further details on ICP-MS analysis may be found in Ref. [7]. The detection and quantification limits are isotope dependent, but typically fall in the low to high ppt (ng dm^{-3}) range, with an error limit of ~20%. In addition to the ICP-MS analysis, the Cs-137 concentration was measured with γ-

spectrometry. A one-point calibration was made with a 1.8 MBq (~31 ppb Cs-137) solution.

3. Results and discussion

As discussed in section 1 above, the release of elements distributed in the UO_2 matrix (i.e. category 4 or 5 according to Ewing 2015 [5]) is expected to be governed by the dissolution of the UO_2 matrix. To investigate this, we compare the fractional release rate of U-238, Eu-153, Nd-144 and Sr-90 from leaching of segments to the release during leaching of fuel fragments (Figs. 1—4).

The fractional release rates are determined by calculating the fraction of inventory in aqueous phase (FIAP) as a function of leaching time), based on the results from the ICP-MS measurements and radionuclide inventory of the fuel. The radionuclide inventory of the fuel used in this study is presented in Ref. [7]. The

FIAP is divided by the time for each contact period to obtain the release rate. As vessel stripping was only performed for the segment leaching all release data below is based on FIAP only and does not take into account the fraction of radionuclides sorbed to the vessel walls.

The results from the vessel stripping has been thoroughly evaluated in ref 7. It is clear that the lanthanides as well as curium and plutonium exhibit strong sorption, whereas technetium, cesium, iodine, molybdenum and strontium are not sorbed [7].

As can be seen in Fig. 1 the release rate of U-238 is higher for fuel fragments than for segment samples during the duration of the experiments. It can also be noted that in the case of segment samples the release rate of U-238 tends to stabilize between $1 \times 10^{-7} \, d^{-1}$ and $1 \times 10^{-8} \, d^{-1}$ at the end of the experiments (~1900 days), this stabilization of the release rate is not observed for the fuel fragments where the experiments were terminated after ~1150
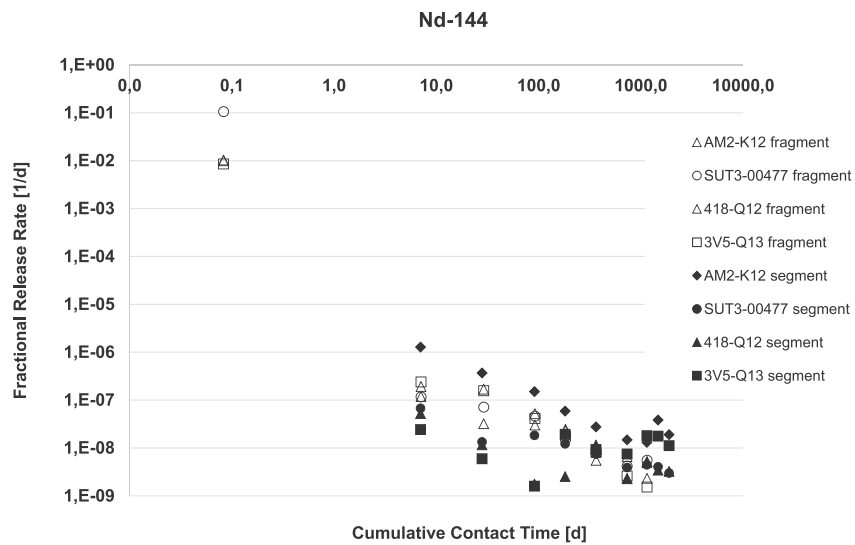

Fig. 4. Fractional release rate of Nd-144 as a function of cumulative contact time.
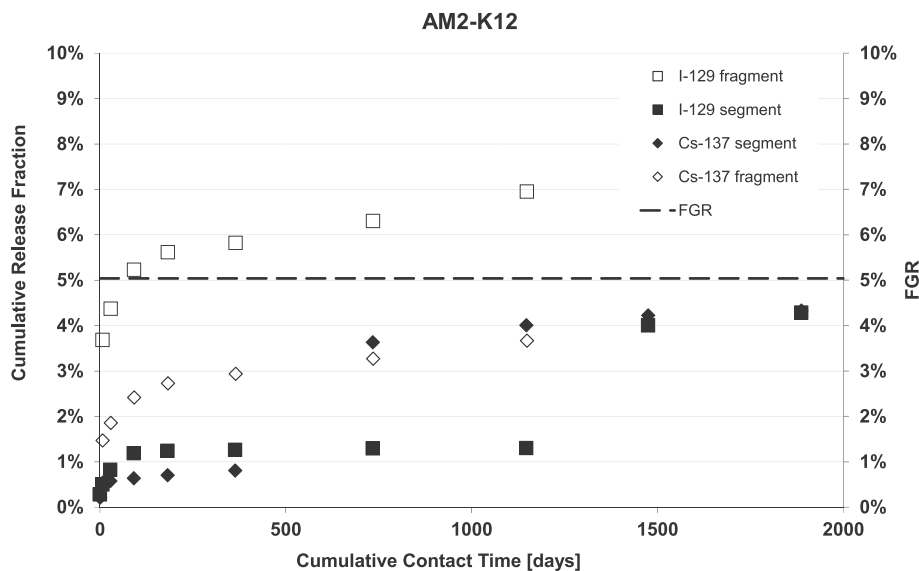

Fig. 5. Cumulative fractional release of I-129 and Cs-137 as a function of cumulative contact time for fuel sample AM2-K12.

days leaching.

The results show that for the fragment leaching the Sr-90 (Fig. 2) release is nearly one order of magnitude higher than the U-238 release and The releases of Eu-153 (Fig. 3) and Nd-144 (Fig. 4) are around one order of magnitude lower than the U-238 release. One reason for the low measured release of lanthanides is that a significant part of the released lanthanides is found in the vessel strip solutions, partly because some fuel particles have been dissolved, but also because the nuclides of concern had been absorbed by the vessel walls. The fraction of the released radionuclides sorbed to the vessel walls would not be visible in the FIAP. This has been demonstrated and discussed in Ref. [7]. Another reason could be that during the oxidative dissolution of UO_2, the release of oxidized U(VI) is not necessarily accompanied by the release of elements such as Eu and Nd, which cannot be oxidized to a higher state and can have a slower rate of desorption until they are removed by excavation of surrounding U cations as discussed by Hanson and Stout [16]. Further, the 3-valent cations which cannot be oxidized serve as effective negative charges, making more difficult for the nearest neighbor uranium ions to oxidize. This reduces the number of donor acceptor sites for oxidant reduction at the surface, thus decreasing the rate of oxidative matrix dissolution. As in the case of U-238, the release rates of Eu-153, Nd-144 and Sr-90 continue to decrease throughout the experiments. For the segment leaching the data is scattered and it is more difficult to distinguish clear trends. However, in general the Eu-153 and Nd-144 release rates are in the same order of magnitude or lower than the U-238 rate whereas also in this case the Sr-90 release rate is one order of magnitude higher than for U-238.

The higher release rates of U-238 and other matrix elements from fragments compared to segments can be attributed to a larger surface area being exposed to the leaching solution. The results presented here indicate that this increase in surface area increases the matrix dissolution rate by around one order of magnitude. The results from the segment leaching agree with literature data for example the study of Gonzalez-Robles et al. [17] where the authors find lanthanides to be released congruently with the UO_2 matrix whereas Sr, Cs and Mo are found to be released at a higher rate. However, the data for fragment leaching presented here indicate that also the release of lanthanides may be in-congruent in some cases, potentially due to the excavation effect discussed above.

In order to further explore this effect and to eliminate the effect of exposed surface area, the Nd-144 and Eu-153 non-cumulative release can be normalized to the release of U-238. The result of this normalization is presented in Table 3 as percentage of U-238 release. As can be seen in the table the release of Nd-144 and Eu-153 is in general in the order of a few percent of the U-238 release during the leaching of fragments. For the segments the data is more scattered as mentioned above, however one can nevertheless note that the release of Nd-144 and Eu-153 reaches congruent release (i.e. 100%) or higher in many cases.

It is somewhat surprising to see that the sample type seems to affect the congruence ratios of Nd-144 and Eu-153. A potential explanation for this would be that a larger surface area (as in the case of fragment leaching) leads to a higher degree of pre-oxidation (i.e. higher degree of U release relative to Nd/Eu) of the samples due to the exposure to air prior to the leaching experiment. It can also be noted that the release relative to U-238 is consistently higher for Eu-153 than for Nd-144. This is surprising as both nuclides are expected to have similar matrix distribution and release properties.

In a leaching experiment, the instant release of segregated elements is generally considered to occur within the first weeks or

Table 3
Release of Nd-144 and Eu-153 presented as percentage of U-238 release for each contact period (pre-washing excluded).

Contact period	4I8-Q12				SUT3				3V5-Q13				AM2-K12			
	Nd-144		Eu-153		Nd-144		Eu-153		Nd-144		Eu-153		Nd-144		Eu-153	
	segment	fragment	segment	fragment	segment	fragment	segment	fragment	segment	fragment	segment	fragment	segment	fragment	segment	fragment
2	4%	1%	43%	7%	2%	1%	4%	4%	2%	4%	7%	8%	84%	4%	194%	38%
3	3%	4%	21%	9%	2%	3%	7%	6%	3%	7%	22%	15%	70%	2%	120%	19%
4	1%	3%	35%	8%	7%	3%	36%	7%	2%	4%	30%	10%	57%	5%	97%	16%
5	2%	2%	32%	5%	9%	1%	24%	3%	32%	3%	135%	7%	78%	5%	143%	18%
6	12%	1%	85%	2%	12%	1%	36%	2%	24%	1%	50%	3%	55%	2%	109%	12%
7	8%	1%	23%	2%	8%	2%	22%	3%	29%	1%	64%	2%	29%	2%	168%	4%
8	8%		23%		9%		23%		82%		166%		19%		63%	
9	6%		12%		7%		16%		97%		193%		55%		137%	
10	5%		11%		6%		18%		60%		104%		55%		110%	

months up to around 1 year of water contact [11]. The data from the initial part (~1 year) of the present leaching experiments are discussed in previous publications [10,11]. It is concluded that the releases of Cs and I from segment samples are systematically lower than those from fuel fragments during the same time interval for high burnup samples (58−75 MWd/kgU), which can be attributed to the closed fuel-cladding gap inhibiting the exposure of the gap inventory to water.

In Ref. [11] the data from the present leaching series are presented together with data obtained at the laboratory of PSI (Paul Scherrer Institut, Switzerland). The general conclusion from this publication is that the Cs-137 release data supports the suggested ratio of fractional release to FGR of $1/\sqrt{3}$ and that the I-129 release appears to be in the order of FGR or slightly lower.

In this paper we present data for the full leaching time, up to 1888 days and 1149 days for segments and fragments respectively. Figs. 5−8 show the cumulative release fractions of Cs-137 and I-129 as a function of leaching time for the fuels used in this study. During these longer leaching periods it is possible to observe that in some

cases a sudden sharp increase in the Cs-137 and I-129 release occur during segment leaching. As discussed above, cesium and iodine are in general enriched in the gap region due to migration during reactor operation. For the high burn-up fuels used in this study, the gap is expected to be closed and the exposure to leaching solution is therefore limited in the case of segment leaching. A potential explanation for the sudden, sharp increases in cesium and iodine release is that, during the experiment, pathways to the gap are opened enabling the leaching solution to access fresh surfaces, rich in cesium and iodine and thereby cause an increase in the fractional release.

This phenomenon is observed for the two highest burn-up fuels used in this study; for AM2-K12 (75 MWd, Fig. 5) where a sharp increase in Cs release is observed after 360 days leaching and a sharp increase in I release after 1147 days leaching and for 3V5-Q13 (66 MWd, Fig. 6) where a sharp increase in iodine release is observed after 91 and 365 days leaching.

Exploring the fractional release rates for Cs-137 and I-129 (Figs. 9 and 10), it can be noted that for the fragment leaching, both
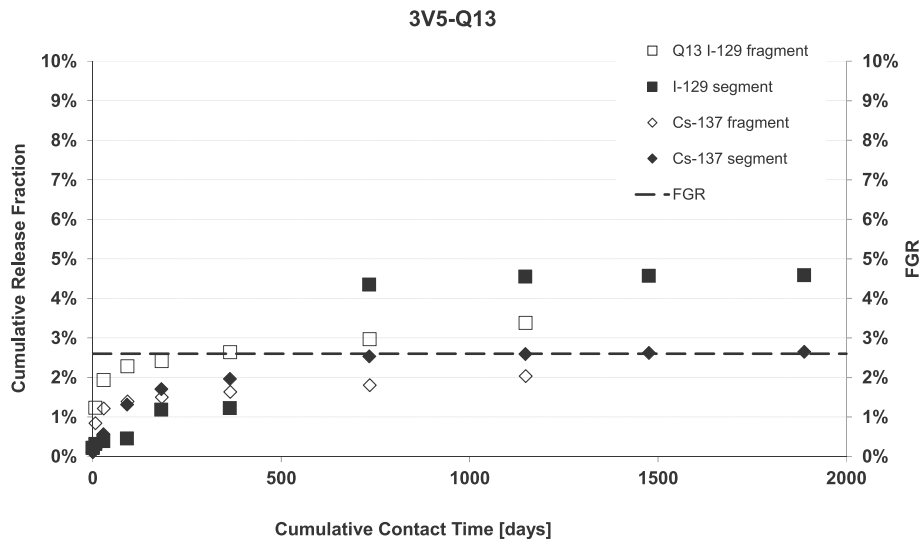

Fig. 6. Cumulative fractional release of I-129 and Cs-137 as a function of cumulative contact time for fuel sample 3V5-Q13.
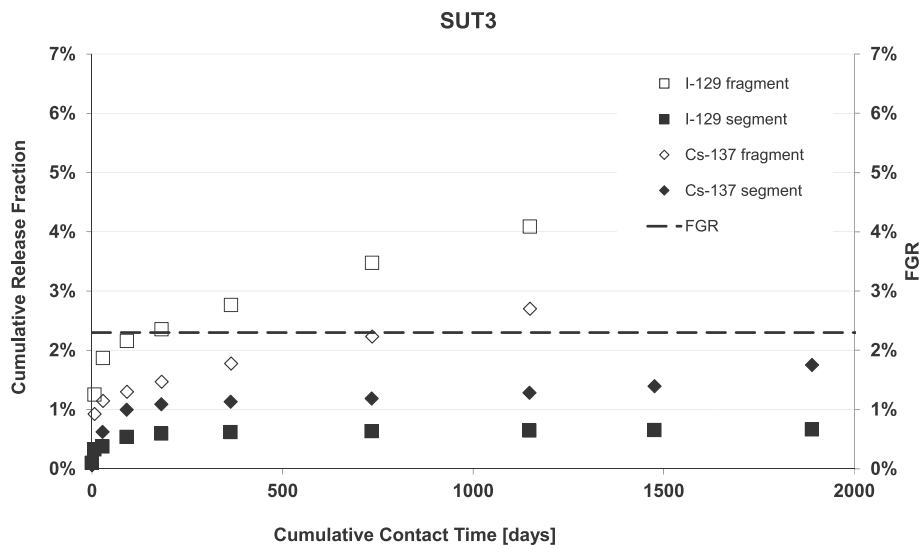

Fig. 7. Cumulative fractional release of I-129 and Cs-137 as a function of cumulative contact time for fuel sample SUT3.
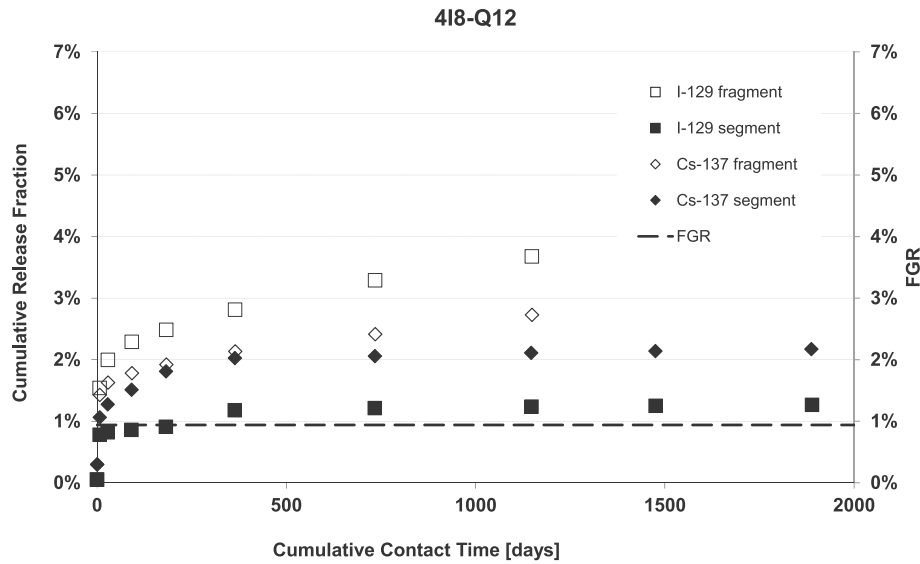
Fig. 8. Cumulative fractional release of I-129 and Cs-137 as a function of cumulative contact time for fuel sample 4I8-Q12.
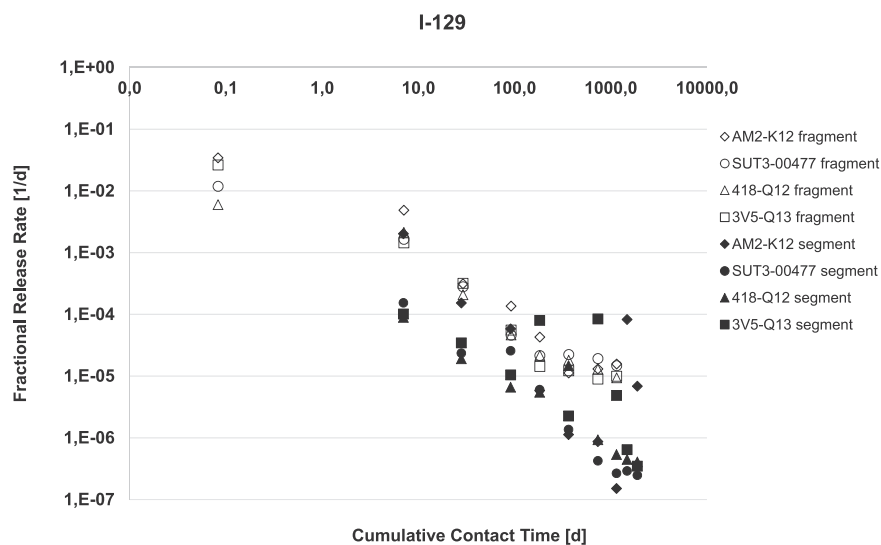

Fig. 9. Fractional release rate of I-129 as a function of cumulative contact time.

the I-129 and the Cs-137 release rates tend to stabilize around 1×10^{-5} d^{-1}. For the segments, the data is more scattered which at least to some extent can be attributed to sudden access to fresh surfaces as discussed above. Ignoring the most pronounced leaps in release rates, the segment leaching experiments tend to give long term I-129 release rates between 1×10^{-6} to 1×10^{-7} d^{-1} and Cs-137 rates between 1×10^{-5} to 1×10^{-6} d^{-1}.

Molybdenum (partly) and technetium are also segregated from the UO_2 matrix and generally are main components of the metallic ε-particles found in large quantities as <8 nm particles in the gap/rim region and metallic particles at grain boundaries. In Figs. 11 and 12 the fractional release rates of Mo-100 and Tc-99 are presented and a clear difference between the release rate from segment samples and fuel fragments can be noted. The release rates are around 10^{-7} d^{-1} for segments and around 10^{-5} d^{-1} for fragments at the end of the leaching period.

The significantly lower release of Mo-100 and Tc-99 from the segment samples is considered to be due to the closed fuel-cladding gap in the high burn-up fuels used in this study. The closed gap prevents the access of leaching solution to the rim-region enriched in small metallic particles containing molybdenum and technetium, limiting the leaching of those elements from the segment samples whereas for the fragment samples the gap/rim-region is fully accessible to the leaching solution.

Comparing with the previous 280 days leaching experiments with 2 cm spent fuel segment (47 MWd/kgU burnup and previously oxidized in an aerated leaching experiment) in 350 mL in 350 mL 10 mM NaCl, 2 mM $NaHCO_3$ solution flushed with Ar+0.03 CO_2 conducted in the Studsvik hot cell laboratory [14], the leaching rates of U-238, Tc-99, Mo-99 and Cs-137 in the present experiment with spent fuel segment (52 MWd/kgU burnup) under aerated conditions are similar (considering experimental errors and
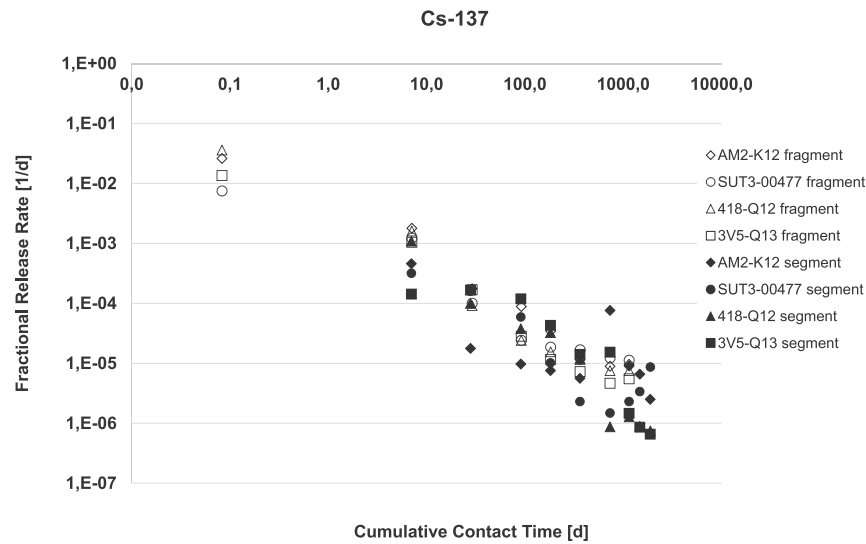
Cs-137

Fig. 10. Fractional release rate of Cs-137 as a function of cumulative contact time.
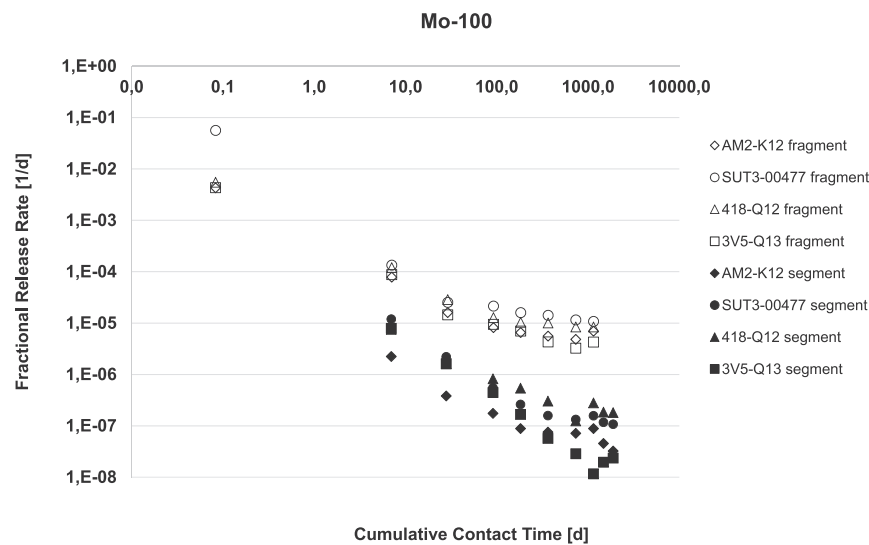
Mo-100

Fig. 11. Fractional release rate of Mo-100 as a function of cumulative contact time.

difference on burnup of nuclear fuel segments used).

Comparing the release rates of the segregated elements discussed here to the fractional rate of U-238 release it is clear that also beyond the initial phase of very rapid release, the segregated elements are released incongruently with the UO_2 matrix. This is particularly evident for the fragment leaching where the release of the segregated elements level of at 10^{-5} d^{-1} whereas the U-238 release rate continue to decrease below 10^{-6} d^{-1}. A potential explanation for this is that during the leaching the fuel matrix dissolves continuously exposing fresh grain boundaries to the leaching solution. The evolution of the fuel during leaching can also lead to exposure of smaller cracks, pores and bubbles within the fuel fragments that were closed at the initial contact with water. The rapid release of segregated elements from these emerging fresh parts of the fuel adds to the radionuclide inventory released by matrix dissolution leading to incongruent dissolution rates.

The powder leaching (simultaneous grinding and leaching) experiment was designed to assess the inventory of Cs and I in the grain boundaries. The experiment was performed using fuel fragments that had undergone 1149 days of leaching prior to the powder leaching and the powder leaching itself added less than 1 h to the total contact time with aqueous solution. The results of the parallel leaching of fuel fragments without grinding, performed to assess the contribution of pre-oxidized phases revealed very low fractional releases and no correction for pre-oxidized phases were made in the results from the powder leaching.

In Fig. 13 SEM images of the powder resulting from the simultaneous grinding and leaching are shown. The aim of the grinding was to reduce the fuel fragments to grain size. The SEM investigation releveled that procedure resulted in grain size (<20 μm)
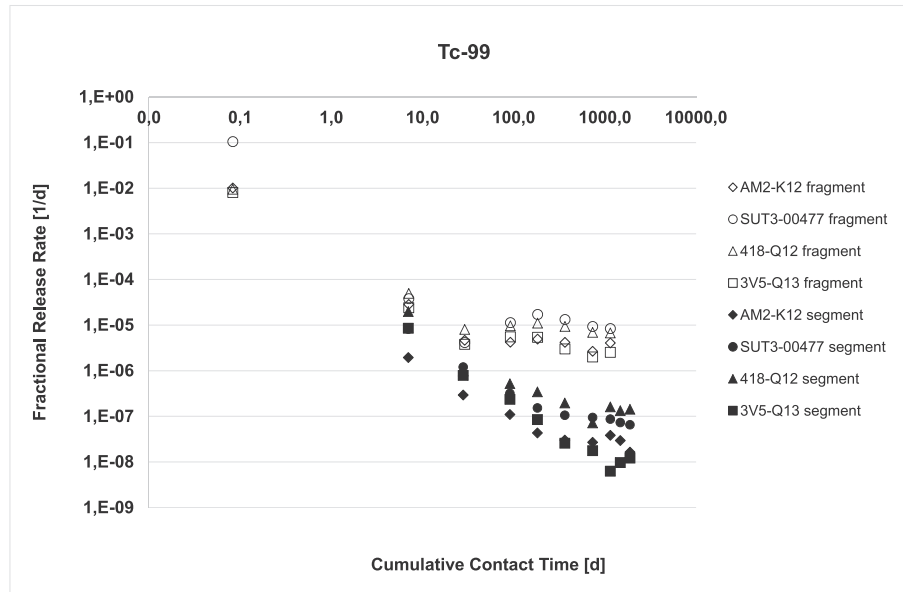
Fig. 12. Fractional release rate of Tc-99 as a function of cumulative contact time.
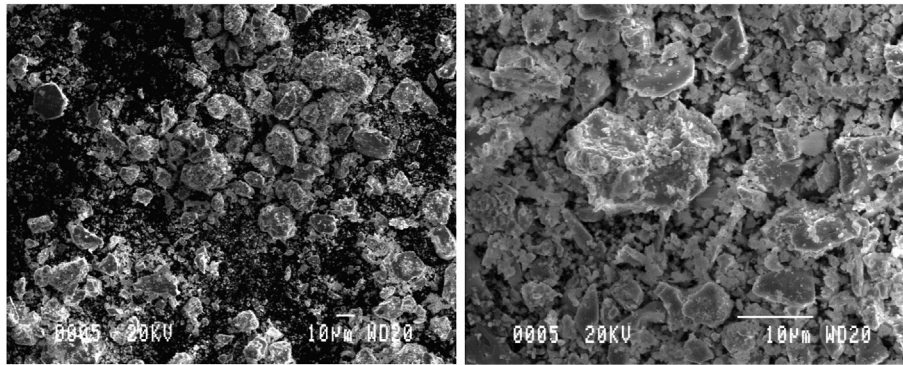

Fig. 13. SEM images of powder from powder leaching experiment, fuel sample AM2-K12.

particles as aimed. There is however also a significant amount of fuel of sub-grain size (<1μm) resulting from the grinding.

The fractional release of Cs-137 and I-129 from the powder leaching was found to be 1.5% and 1.8% respectively. For Cs, this is consistent with the findings in Ref. [18] where the grain boundary inventory of Cs is determined to be generally slightly less than 1% (independent of FGR) and the work of Roudil et al. [19] where the Cs inventory was determined to ~1.4%. In the study of Gray et al. [18] the gap release of iodine is significantly higher (~8%). The fuels used by Gray was however of low density (~10.1 g cm^{-3}) and displayed comparably high FGRs (up to 18%). The fuels used in the present study have initial densities ranging from 10.44 to 10.50 g cm^{-3} and are more representative for commercial light water reactor fuels.

4. Conclusions

In this study, radionuclides release rates from high burnup spent fuel samples in contact with water has been determined for total leaching times up to ~5 years. The aim of the study was to investigate how sample preparation, and thereby access of water to various parts of the fuel, affect the leaching behavior.

We have found that leaching of fuel fragments leads to higher release rates of U-238 and other matrix elements from fragments compared to segment leaching. This can be attributed to a larger surface area being exposed to the leaching solution. The results from the leaching of fuel segments reveal congruent release of e.g. europium and neodymium whereas the release of those elements was lower than the U-238 release for the fragment samples. The lower release could potentially be explained by an excavation effect [16].

The release rates of elements segregated from the fuel matrix was in general found to be lower from segments samples compared to fragment samples, which can be attributed to the closed fuel-cladding gap inhibiting the exposure of the gap inventory to water for the high burnup fuels used in this study.

During leaching of fuel segments, sudden "leaps" in the iodine and cesium concentrations were observed. A potential explanation this behavior is that, during the experiment, pathways to the gap are opened enabling the leaching solution to access fresh surfaces, rich in cesium and iodine and thereby cause an increase in the fractional release. From the results of this study it is evident that also beyond the initial phase of very rapid release, the segregated elements are released incongruently with the UO$_2$ matrix. This too can be explained by the evolution of the fuel during leaching leading to exposure of fresh surfaces to the leaching solution.

Leaching of fuel powder (by simultaneous grinding and

leaching) aimed at assessing the inventory of Cs and I in the grain boundaries. The results showed that the fuel (~78 MWd/kgU) was reduced to grain size or below during the procedure. The fractional release of Cs-137 and I-129 from the powder was found to be 1.5% and 1.8% respectively.

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical limitations.

Acknowledgements

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