Applied Geochemistry 178 (2025) 106234

Contents lists available at ScienceDirect

Applied Geochemistry

journal homepage: www.elsevier.com/locate/apgeochem

Radionuclide release from spent nuclear fuel in sealed glass ampoules

Lena Z Evins [a,*], Charlotta Askeljung [b], Alexandre Barreiro Fidalgo [b], Anders Puranen [b], Olivia Roth [a], Kastriot Spahiu [a]

[a] Swedish Nuclear Fuel and Waste Management Co., Evenemangsgatan 13, Box 3091, 169 03, Solna, Sweden
[b] Studsvik Nuclear, Nyköping, Sweden

ARTICLE INFO

Editorial handling by Horst Geckeis

Keywords:
Spent nuclear fuel
Radiolysis
Radionuclides
Dissolution

ABSTRACT

Radiation from spent nuclear fuel affects the redox chemistry of water in the proximity of the fuel surface. The overall effect of the radiolysis is oxidizing so that U(IV) in the spent nuclear fuel is oxidized to U(VI). The dissolution of U(VI) is relatively fast, especially when the water contains bicarbonate. Based on this, radiolytic oxidation is considered the main driving force for spent fuel dissolution and radionuclide release in a spent fuel repository environment, and many studies over the years have aimed to further our understanding of this process and how it is influenced by available redox active components in open and closed systems. Here, data from sealed glass ampoules in which spent fuel is leached for one and five years, are compared with published data from a previous similar experiment. With regards to evolution of radiolytic gases, the results are comparable to the results from the previous experiments: a steady state with regards to oxygen and hydrogen composition is observed. An unexpected observation is that some ampoules with old, pre-oxidized fragments produced less radiolytic gases. These older fragments release a larger fraction of the radionuclide inventory of the samples, yielding concentrations that are on the same level as previously published data. The data from the old fragments presented here are affected by the pre-oxidation and prolonged washing procedure, which confounds the interpretation of those data. New, recently prepared fragments yield data that are easier to interpret. The radionuclide concentrations in the ampoules with new fragments are much lower; uranium concentrations of ca 5E-6 M after one year, and ca 3E-5 M after five years. Using the calculated radionuclide inventory in the fuel samples, an apparent radionuclide release rate in these initially anoxic systems, based on U release, is ca 3E-5 per year.

1. Introduction

In a spent nuclear fuel repository, dissolution of the spent fuel UO_2 matrix is the process which would release the majority of radionuclides into the environment, in case water enters a failed spent fuel canister. The UO_2 dissolution rate is strongly influenced by uranium oxidation, increasing the solubility of the spent fuel with orders of magnitude. In a reducing environment, oxidation of the spent fuel may still happen due to radiolysis. Even though radiolysis will produce both molecular oxidants (eg O_2, H_2O_2) and reductants (eg H_2), at room temperature the H_2 reacts slowly and can be considered to be inert in the absence of catalysts, giving an overall expected oxidative effect of radiolysis. Therefore, efforts have been directed towards understanding the fate of the radiolytic oxidants, mainly H_2O_2, that are produced on and near the surface of spent nuclear fuel. It has been known for some time that the galvanic coupling between the metallic alloy particles and the spent fuel matrix allows electrons from adsorbed H_2 to reduce uranium oxidized by H_2O_2 (Broczkowski et al., 2010; Trummer and Jonsson, 2010). The net effect is a recombination of H_2 and H_2O_2 to form water rather than the oxidation of uranium by H_2O_2. Another route for recombination of H_2 and H_2O_2 is via catalytic dissociation of hydrogen peroxide on the surface of the spent fuel (Nilsson and Jonsson, 2011). As the H_2O_2 splits to form two OH radicals, the H_2 can react with these and form H_2O and H. Using deuterium to trace the hydrogen reactions, it was shown that this is part of the explanation of the hydrogen effect (Bauhn et al. 2018a, 2018b).

To follow the radiolysis and the production of radiolytic gases (O_2, H_2) in a closed system, early previous experiments were designed using sealed glass ampoules (Bruno et al., 1999; Cera et al., 2006). A number of ampoules, in which spent fuel fragments were in contact with

---

* Corresponding author.
E-mail address: lena.z.evins@skb.se (L.Z. Evins).

https://doi.org/10.1016/j.apgeochem.2024.106234
Received 19 June 2024; Received in revised form 3 October 2024; Accepted 19 November 2024
Available online 25 November 2024

bicarbonate-containing water under an Ar atmosphere, were produced. These were opened and the gases and liquids analysed at certain chosen points in time; long-contact experiments provided data for 400–900 days, ie up to ca 2.5 years (Cera et al., 2006). The results from these previous long-contact experiments indicated that uranium oxidation appeared to stop after a first initial phase; both the uranium and the radiolysis products H_2 and O_2 stay at constant levels over several years. Thus, in spite of ongoing radiolysis, it appeared that the uranium and other radionuclides were only released in the beginning and no further release was observed over the experimental timescale. This apparent steady state condition over long times (years) was, however, not the predicted result based on the radiolytic model that was developed at the time (see Appendix in Cera et al., 2006), indicating the need for a more complicated surface reaction mechanism. Further work in this respect improved the model (Eriksen et al., 2008), in particular with regards to effects of noble metal particle catalyzed H_2 reduction.

Many experiments have confirmed that oxidation of uranium in spent nuclear fuel can be strongly suppressed in the presence of excess H_2 (eg Spahiu et al., 2004; Carbol et al., 2009; Puranen et al., 2018; Ekeroth et al., 2020). The H_2 pressure required for this effect depends on the radiation intensity. Jonsson et al. (2007) concludes from modelling that the radiolytically produced hydrogen from a 1000 year old spent fuel is enough; however for existing spent fuel samples, no more than a few decades old, it seems that radiolytically produced hydrogen alone is not enough (Puranen et al., 2020). However, the interpretation of the previous ampoule data (Cera et al., 2006) was that radiolytic H_2 production was sufficient in these systems (Eriksen et al., 2008). Taking the hydrogen effect into account, modelling indicates that radiolytic hydrogen alone (ie, no initial H_2) can suppress UO_2 oxidation if the fuel is older than 100 years (Jonsson et al., 2007). The more recent modelling results of Hansson and Jonsson (2023) support this conclusion, showing that radiolytic hydrogen alone is efficient at reducing oxidative uranium dissolution at a dose rate of 10 Gy/h (2.78E-3 Gy/s). Clearly, the observation of steady state and apparent suppression of uranium oxidation in the ampoules of Cera et al. (2006) triggered questions, for example if the observed effect is temporary or if it would be observable also in longer running experiments. Therefore, in 2016, a new set of ampoules were made with the plan to open them after 1, 5 and 10 years. Data from 1-year and 5-year ampoules are now available and are presented and discussed in this contribution.

2. Materials and methods

2.1. Fuel samples

The studied fuel fragments originate from a BWR fuel rod that was irradiated in Ringhals (R1) called 33–25046. This rod was irradiated between 1980 and 1992 and reached a burnup of ca 60 MWd/kgU, which was unusually high for that period. The extended irradiation period and high burnup was reached since this rod experienced two “lives” by being transferred from one assembly to another. The measured rod puncture fission gas release was 2.4%. This fuel is the same as in the previous study (Cera et al., 2006; Note that the correct fuel ID for long contact time experiments is provided in Appendix 1, section 3.1). In fact, some fragments used in the current study were prepared for the previous study, which means that they were separated from the rod in 2003 or earlier. Some of these old fragments were previously washed in 10 mM bicarbonate ca 10 years ago as preparation for a separate project, but were not leached in any previous experiment. The old fragments were stored in an Ar container in the Hot Cell, which was not completely airtight. For the current study new fragments were also collected from freshly crushed material. The local burnup at the sample selection site was estimated to 65 MWd/kgU from the rod axial gamma profile; this value was used to calculate the radionuclide inventory (Zakova, 2018; Supplementary data).

For each ampoule, ca 1 g fuel fragments of the size 2–4 mm were used. Regarding old fragments, no distinction was made between fragments that were previously washed and not, meaning a mixture of these were loaded into the ampoules with old fragments. To remove oxidized uranium and radionuclide inventory associated with this oxidized fraction, the fragments were washed using repeated exposure to water with 10 mM bicarbonate in separate glass vessels. The uranyl carbonate complexes formed ensure that oxidized U is efficiently dissolved from the sample surface. Both old and new fuel fragments were washed; however, it was noted that the old fragments required an extended washing time in order to reach an acceptably low U release (4–8 μM U in the wash solution). Due to a mistake the washing of ampoule nr 7 was interrupted prematurely.

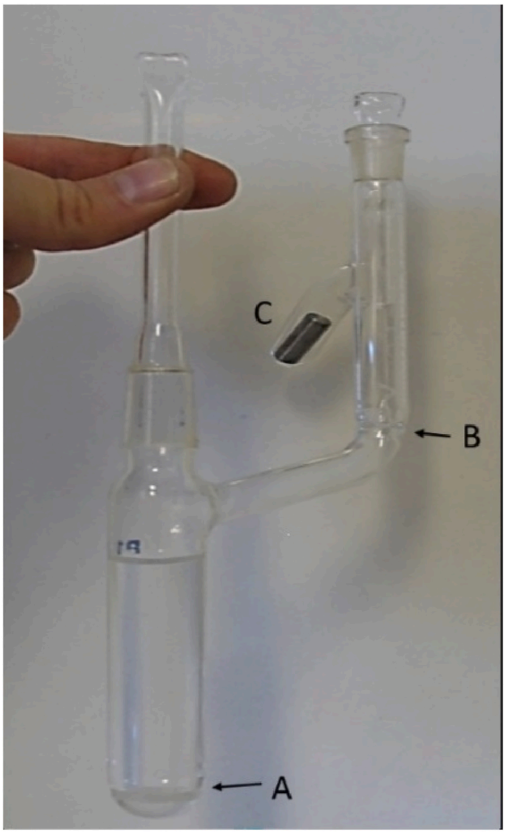

Fig. 1. Glass ampoule (no fuel added). A: Glass frit in bottom, B: glass membrane, C: steel plunger.

2.2. Ampoules

Sealing the ampoules involved the following procedures. In the hot cell, the fuel fragments were washed in 10 mM bicarbonate, prepared by dissolving corresponding amount of $NaHCO_3$ (99.7–100% purity) in ultrapure water, under Ar bubbling to remove oxidized uranium. This is also how the bicarbonate was prepared for the leaching solution; no pH adjustment was done and the measured pH was 8.8 initially. The washed fragments were transferred to the glove box with inert atmosphere (approximately Ar 94%, He 5%, 1% N_2 and 1 ppm O_2) and placed on a glass frit on the bottom of the ampoules (see Fig. 1). Then 30 ml of leaching solution was added. The ampoules were then flushed and sealed in Ar with ~5% He; the sealing was done by melting the glass in the neck of the ampoule. The steel plunger seen in the upper right part is used for cracking the seal when sampling the accumulated gas. For sampling, a magnet is used to move the steel plunger (Fig. 1) so that it is dropped on the glass membrane, cracking it and thus releasing the gas for analysis with gas mass spectrometry.

The current study concerns the seven ampoules listed in Table 1.

Table 1
Ampoules analysed in the current study. Old fragments = previously prepared fragments. New = Newly prepared fragments.

Ampoule #	Sealed (date)	Leaching time (years)	Leaching time (days)	Fuel fragments	Fuel (g)	Washing time (days)	Aqueous solution	O_2 in glove box (ppm)
3	May 3, 2016	1.35	493	Old	1.06	9	10 mM NaHCO3	2
5	May 3, 2016	1.34	490	Old	1.06	9	10 mM NaHCO3	2
6	May 31, 2016	1.27	464	New	1.06	4	10 mM NaHCO3	1
10	May 31, 2016	1.28	469	New	1.07	4	10 mM NaHCO3	1
7[a]	April 20, 2016	5.15	1880	Old	1.05	2	10 mM NaHCO3	1
11	June 16, 2016	5.02	1832	New	1.08	4	10 mM NaHCO3	1
13	June 16, 2016	5.18	1889	New	1.05	4	10 mM NaHCO3	1

[a] fragments were insufficiently washed ([U] in wash solution reached 4.2E-5 M).

Table 2
U concentrations (mol/L) in wash solutions (Scintrex data). The duration of each washing step is normally 24 h but may extend to 72 h.

Ampoule #	Wash 1	Wash 2	Wash 3	Wash 4	Wash 5	Wash 6	Wash 7
3	2E-04	5E-05	4E-05	1E-05	1E-05	1E-05	4E-06
5	2E-04	5E-05	4E-05	8E-06	7E-06	7E-06	4E-06
6	5E-07	8E-08					
10	1E-06	2E-07					
7	1E-04	4E-05					
11	8E-07	3E-07					
13	1E-06	3E-07					

These ampoules were sealed in 2016, and then stored in a lead cask at room temperature all together, with no shielding between each other. Four ampoules were opened after ca 1 year of leaching, and three after ca 5 years of leaching.

2.3. Gas and liquid analysis

At the time for sampling of the ampoules, they were transferred to the glove box and connected to a vacuum sampling connection including a vessel to collect the gas sample. The gas was sampled using the procedure described above (section 2.2); the gas thus released was collected in a sampling vessel. The ampoule was then detached from the gas sampling system and 25 ml of the leaching solution was removed using a syringe and a PEEK tube.

The gas was analysed by gas mass spectrometry (InProcess Instruments GAM 400). The liquid samples from the ampoules were analysed for radionuclide content, including U, using inductively coupled plasma mass spectrometry, ICP MS (PerkinElmer Elan II and Nexion 350D). The liquid samples were ultracentrifugated and acidified for ICP-MS analyses. No separate sampling nor sample preparation was performed for I analyses, meaning the I data are only indicative. All wash solutions were analysed for U content with Scintrex (device UA-3); additionally, wash solutions from old fragments in ampoule 3 and 5 were also analysed with ICP MS. The Scintrex analyses are only used for screening, and the uncertainty is higher than for ICP-MS. The analytical uncertainties for the ICP-MS data are generally 10% or less. The uncertainty for the gas data is estimated to 10%.

Analyses of pH and carbonate content of the liquid were performed before and after the experiment. All analyses are performed outside of the glove box. A Thermo Scientific Orion ISE meter is used with two electrodes, one for pH and for carbonate; pH is measured first, then carbonate on the same solution.

3. Results

Data from wash solutions, gas and leach data from the seven ampoules are presented below and compared with relevant data published by Cera et al. (2006). The data chosen from Cera et al. (2006) for comparison are from ampoules with 10 mM bicarbonate in the leaching solution.

Table 3
Total grams (from ICP-MS data) and fraction of sample radionuclide inventory in wash solutions for ampoule 3 and 5. Note that the I data are only indicative.

Nuclide	Ampoule 3 (g)	Ampoule 3, fraction(%)	Ampoule 5 (g)	Ampoule 5, fraction (%)
Sr-90	8.9E-07	0.11%	9.5E-07	0.12%
Mo-100	5.2E-06	0.27%	6.1E-06	0.31%
Tc-99	2.2E-06	0.15%	2.8E-06	0.19%
I-129	1.2E-05	3.41%	3.8E-05	11.05%
Cs-133	4.5E-06	0.22%	5.3E-06	0.26%
La-139	1.2E-06	0.05%	1.4E-06	0.06%
Nd-144	1.7E-06	0.06%	2.0E-06	0.07%
U-238	1.9E-03	0.20%	2.3E-03	0.24%
Np-237	7.2E-07	0.09%	9.1E-07	0.12%
Pu-239	5.1E-07	0.01%	5.6E-07	0.01%

Table 4
Composition of gas phase and aqueous solutions. The gas sample from ampoule nr 3 was lost and therefore not listed in the table.

Ampoule (#)	5	6	10	7	11	13	
Gas							In glove box
Kr (%)	0.02	0.02	0.02	0.04	0.01	0.01	0
Xe (%)	0.1	0.1	0.1	0.3	0.1	0.1	0
H2(%)	0.7	3.1	4.4	0.5	4.2	3.7	0
He(%)	4.7	4.8	4.8	2.4	4.2	2.6	4
N2(%)	0.9	0.7	0.7	1.2	0.3	0.4	1
O2(%)	0.3	1.0	0.6	0.2	1.5	1.2	0
Ar(%)	93.3	90.2	89.4	95.3	89.8	92.0	95
H_2/O_2	2.3	3.2	7.1	2.8	2.9	3.1	0
Aqueous solution							Initial
H_2 (M)	5.6E-06	2.4E-05	3.7E-05	3.9E-06	3.5E-05	3.0E-05	
O_2 (M)	4.2E-06	1.3E-05	8.8E-06	2.3E-06	2.0E-05	1.6E-05	
pH	9.3	9.6	9.6	8.8	9.0	9.0	8.8
Carbonate (M)	1.0E-02	9.2E-03	8.8E-03	1.1E-02	9.9E-03	1.0E-02	9.8E-3

3.1. Radionuclides in wash solutions

The Scintrex measurements of U content in the wash solutions indicate that a higher fraction of U was washed away from old fragments compared with new fragments (Table 2). The follow up on these observations involved ICP-MS analyses of wash solutions from old fragments placed in ampoules 3 and 5. It is apparent from the results (Table 3) that a large part, several %, of the sample inventory of I-129 was washed away from these old fragments. Note, however, that the analysis procedure is not optimized for I analysis since the sample is acidified and therefore the iodine data should be considered indicative only; it is likely an underestimation of iodine in solution. The fraction of Cs that has been washed away from the old fragments is less than 0.3%.

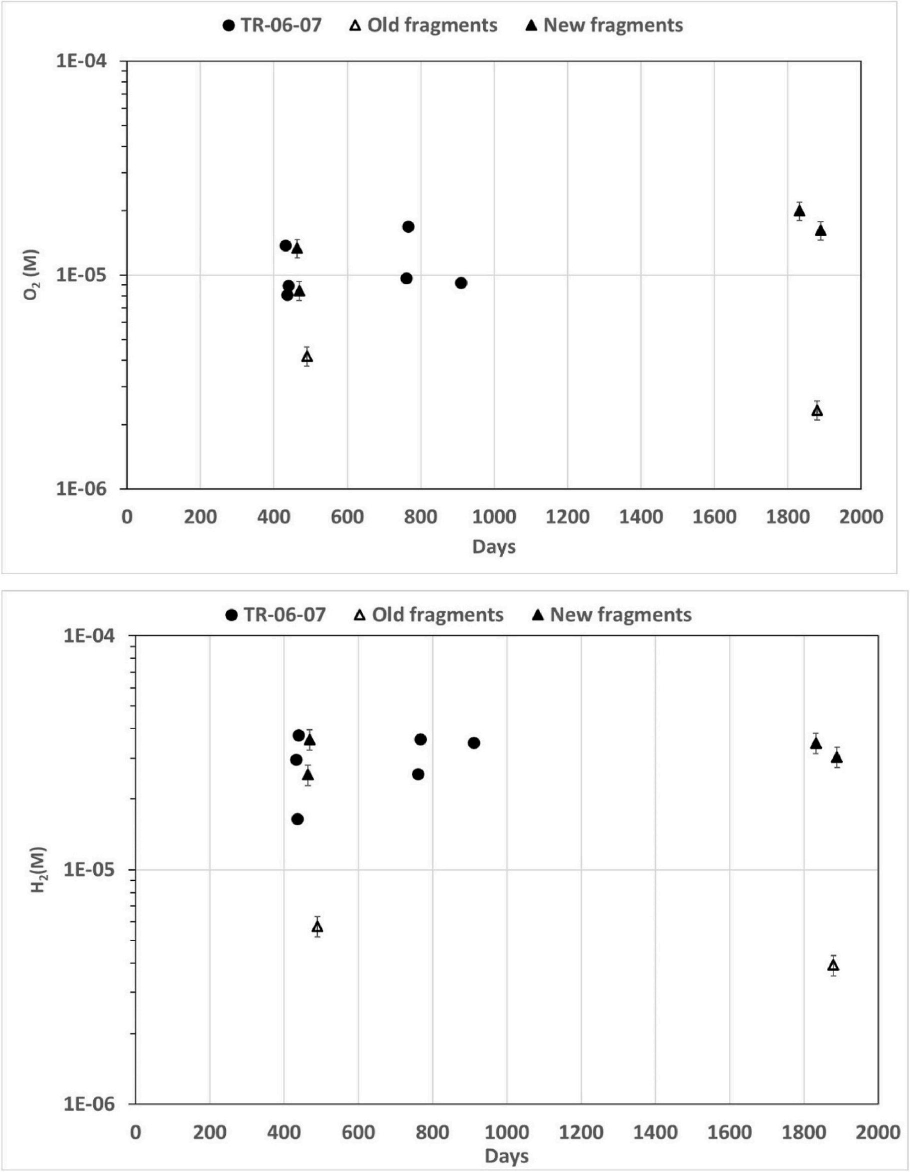

Fig. 2. Top) Oxygen (O_2) concentration in aqueous solution. Bottom) Hydrogen (H_2) concentration in aqueous solutions. TR-06-07: Data from Cera et al. (2006); Old fragments: Previously prepared samples; New fragments: Samples prepared for this study. Error bars on data for old and new fragments correspond to an analytical error of 10%.

3.2. Gas composition and gas concentration in solution

The gas sample for ampoule 3 was lost. Gas data for ampoules 5,6,10 (~one year) and 7, 11,13 (~five years) are given in Table 4. Also given in Table 4 are the gas compositions of the glove box at the time of ampoule sealing, which means this is the initial gas composition in the ampoule. From the tabulated data it is clear that less hydrogen and oxygen was produced in ampoules 5 and 7. To compare with previously published data (Cera et al., 2006), hydrogen and oxygen data is plotted as concentration in aqueous solution (Fig. 2). The concentration data is determined assuming equilibrium between both phases and using Henry's law with data from Young (1981) and Burkholder et al. (2019). Oxygen follows the trend seen in earlier experiments: it stabilizes around a few 10's of μM. With regards to oxygen, it seems some steady state is reached after about a year in this kind of system. Hydrogen also seems to follow the same trend as seen earlier and hydrogen concentration do not increase above ca 30 μM. The plots in Fig. 2 also show clearly the trend that the ampoules with old fragments have accumulated less hydrogen and oxygen compared with those with new fragments but also compared with the old data.

3.3. Actinide and fission product concentrations

The results from the ICP-MS analyses are given for isotopes; here, the data are given as elemental concentrations to allow direct comparison with the data from Cera et al. (2006). The concentrations of all isotopes for an element given in the analysis are added together to give the elemental concentrations. U and Pu concentrations are given in Fig. 3. Ampoules with old fragments (3, 5, 7) have similar U concentrations as reported by Cera et al. (2006), and concentrations seem to remain unchanged for 5 years. The same can be observed for Pu. However, there is a striking difference in both U and Pu concentrations in ampoules with new fragments (6, 10, 11, 13). After one year of leaching the actinide concentrations are more than one order of magnitude lower for the new fragments. After five years, the concentration is still much lower, but, at these lower concentrations, it is possible to discern an increase in concentrations over time. In general, there is a ca 10% uncertainty on the ICP-MS data. The more imprecise Scintrex U data from the wash

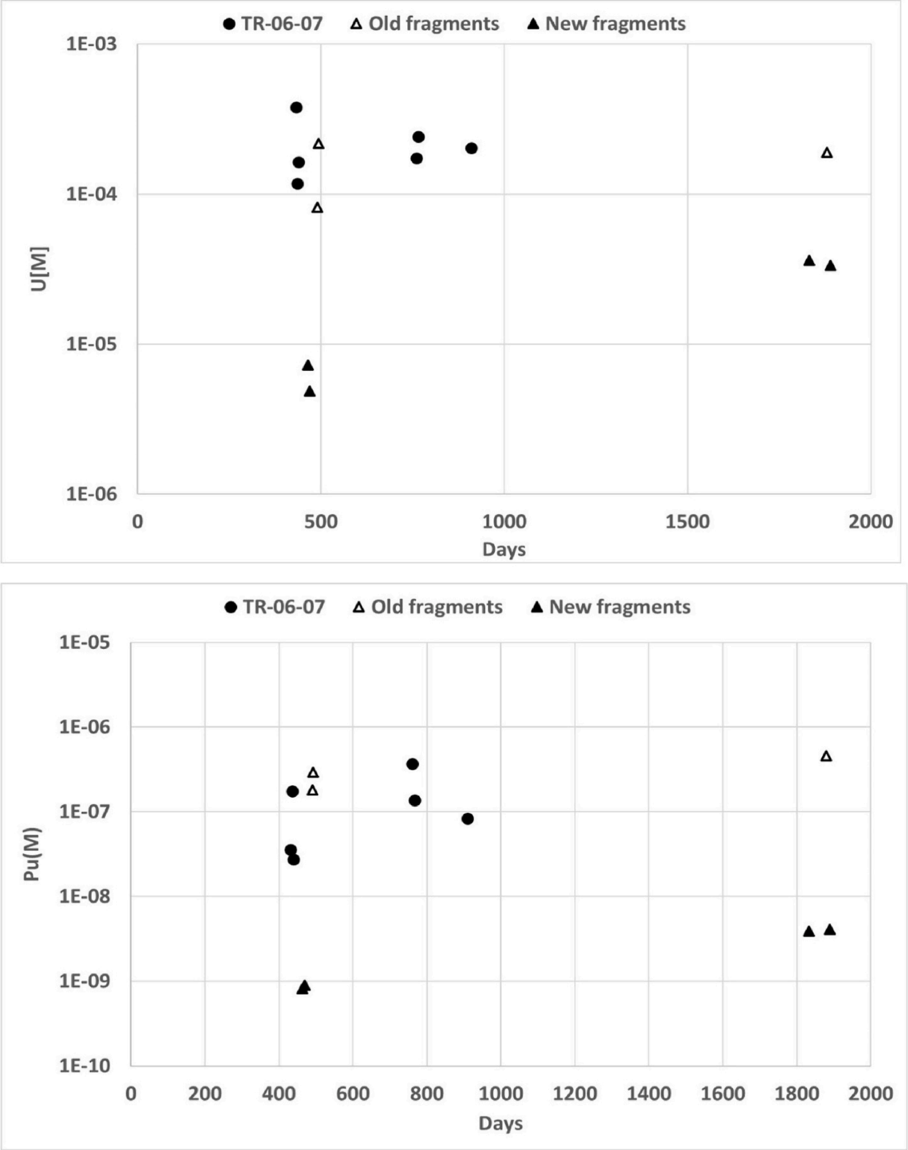

Fig. 3. Top) U concentrations. Bottom) Pu concentrations. TR-06-07: Data from Cera et al. (2006); Old fragments: Previously prepared samples; New fragments: Samples prepared for this study. Estimated analytical error for old and new fragments is ca 10% yielding error bars smaller than the data symbol.

indicated 2 to 4 times higher concentration than the ICP-MS; in any case the Scintrex was only used as a screening method.

The measured concentrations of Sr and Nd (Fig. 4) show similarities with the actinide data, with much higher concentrations in ampoules with old fragments. The trends regarding high mobility, non-redox sensitive fission products Cs and I can be seen Fig. 5. The elemental concentrations are plotted together, however, it should be noted that the inventory of Cs is ca one order of magnitude higher than the inventory of I. Old fragment Cs data seem very similar to the data from Cera et al. (2006) and indicate higher concentrations that do not increase over time. The Cs concentrations from the new fragments are ca one order of magnitude lower, but as opposed to the U, Pu, Sr and Nd data, there is no clear increase over time for Cs. For I, comparison with old data was not possible since I was not measured by Cera et al. (2006). There seem to be a difference in how I is released to solution from old and new fragments; however, the I data are only indicative and based on the washing data (Tables 2 and 3), the I data should be interpreted with caution.

The metals Mo and Tc (Fig. 6) yield quite different results. Mo data are similar to those of Cera et al. (2006), and differences between old and new fragments are not that pronounced. The data for Tc shows another picture and one contrasting with the other results presented here: for Tc, the old fragments are the ones that yield the lowest concentrations. Considering only the new fragments, however, the results are in line with those of Cera et al. (2006).

4. Discussion

4.1. Radiolytic gases

One aim of the study was to provide data for a longer time series than the previous Cera et al. (2006) study, to investigate if the previously observed trend, with no increase in concentrations over time, would remain for longer times. The first observation is that this appears true for the radiolytic gases, O_2 and H_2. For molecular hydrogen to be kept at the same level over several years, even though it is continuously produced by radiolysis, could mean that it has reacted with something in the system. Alternatively, there has been a loss from the system, albeit this seems unlikely. Hydrogen can react with other radiolysis products, either in bulk solution or at the solid-liquid interface (Jonsson, 2022, 2023). Molecular hydrogen is not expected to react with dissolved

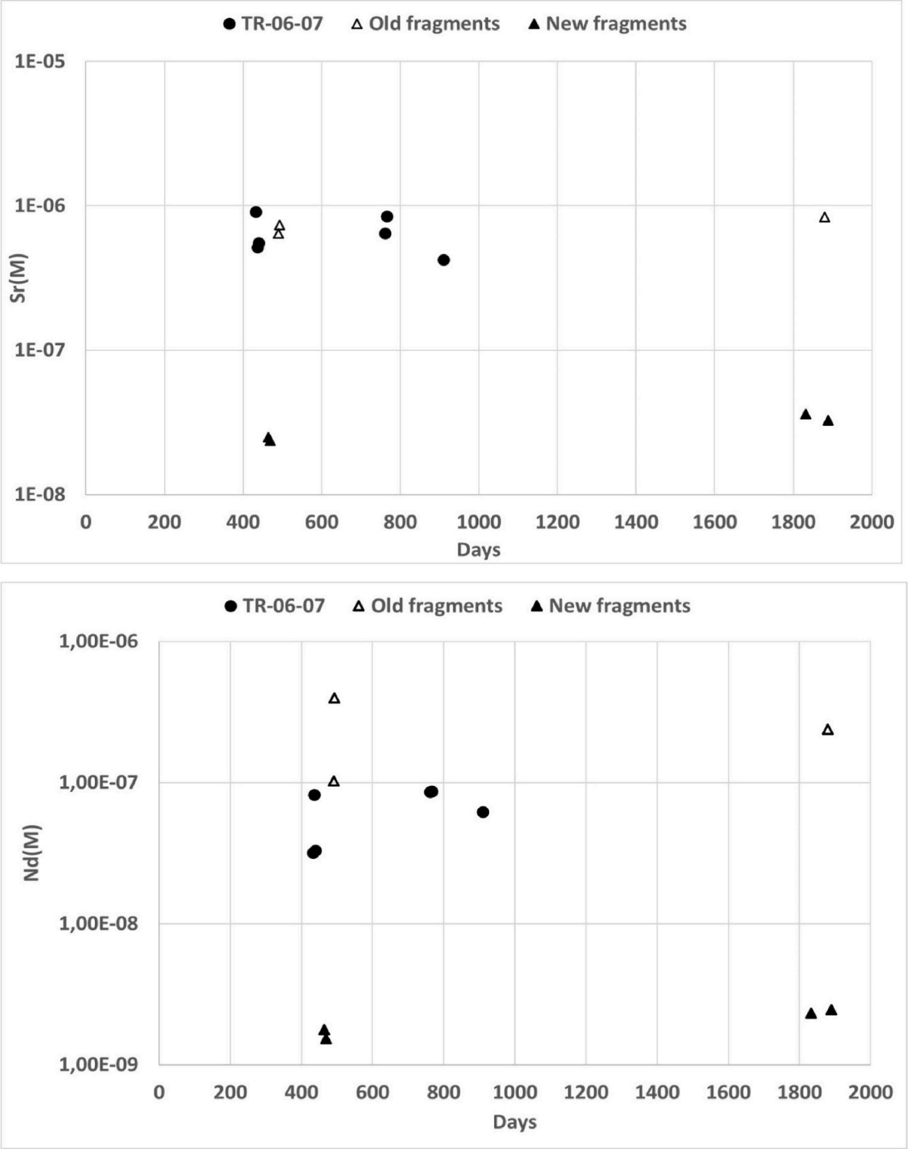

Fig. 4. Top) Sr concentrations. Bottom) Nd concentrations. TR-06-07: Data from Cera et al. (2006); Old fragments: Previously prepared samples; New fragments: Samples prepared for this study. Estimated analytical error for old and new fragments is ca 10% corresponding to the size of the data symbols.

uranium, or other dissolved molecular species, but in the presence of a catalysing surface, molecular hydrogen can be oxidized, thereby reducing other species (eg U(V) or U(VI)). Another relevant reaction catalyzed by actinide oxide surfaces is the recombination of H_2 and O_2 to form water (Icenhour et al., 2004). In either case, it is apparent that some reaction in this system is keeping the molecular hydrogen concentration at a steady concentration. Regarding oxygen it seems a slight increase can be seen for the new fragments, although this is unclear with the current data set. Further data from ongoing studies may help to clarify the long-term evolution of the dissolved gases.

The second observation is that the new fragments yield similar concentrations of O_2 and H_2 as the previous study did. However, for the ampoules with old fragments, the yield of radiolytic gases seem significantly less. The fragments come from the same part of the same fuel rod as was used in the Cera et al. (2006) study. The dose rate should thus be very similar (albeit slightly lower due to a few years of decay) and this is confirmed by the data from the new fragments. The main difference is the history of the fragments, since the old fragments were prepared sometime around or before 2003 – the fragments chosen for our study were a mixture of fragments that had been washed (but not leached) and fragments that had only been crushed and no other water contact than humidity in the hot cell. It is quite likely that the fragments had formed an oxidized layer, as was found during the washing procedure for the current study. The leach data indicates that not all pre-oxidized materials was removed in spite of the prolonged washing, and one hypothesis is that this remaining oxidized layer significantly affects the dose rate to water and thereby the yield of radiolysis products at the interface. This shielding effect would mainly be relevant for alfa-to some extent beta radiation. Another effect of the pre-oxidation and extensive washing is that some fractions of the radionuclides are removed from the sample. As can be seen in Table 3, a fairly large fraction of I was washed out during the prolonged washing of the old fragments, and more Tc-99 and Np-237 were removed via the wash than via the long-term leaching. Another hypothesis therefore is that the removal of radionuclides via washing affected the dose rate to water in the ampoules.

4.2. Radionuclide release

The radionuclide release, as observed by concentration in aqueous solution, is clearly very affected by the history of the fragments. The old

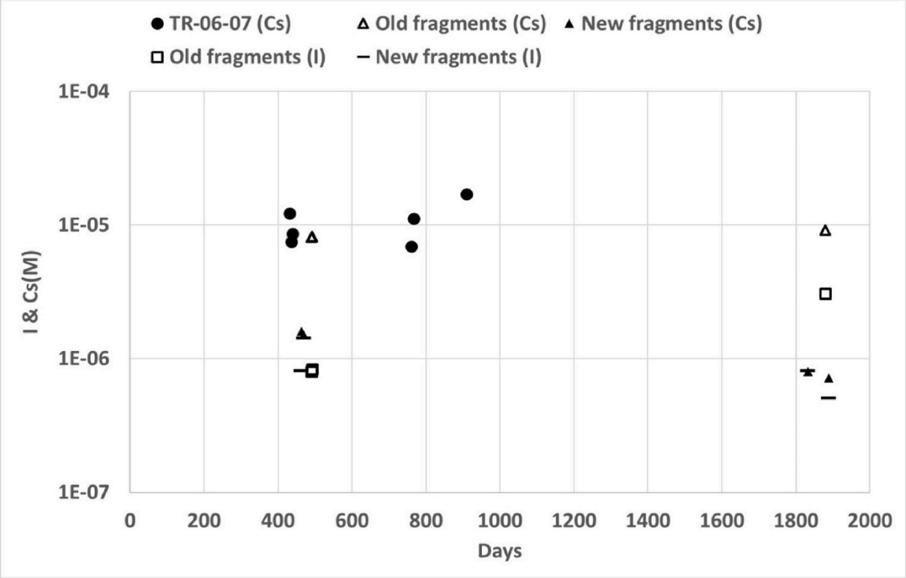

Fig. 5. Cs and I concentrations. TR-06-07: Data from Cera et al. (2006); Old fragments: Previously prepared samples; New fragments: Samples prepared for this study. Estimated analytical error for Cs data for old and new fragments is ca 10% corresponding to the size of the data symbol; I data are only indicative.

fragments give quite different results from the new fragments, for most of the radionuclides studied. Since the old fragments apparently yield less radiolytic gases, one could speculate that this means less radiolytic oxidation and therefore slower radionuclide release. This is however opposite to the observation. The highest concentrations are found for the old fragments; these concentrations are quite similar to those reported by Cera et al. (2006). Presumably, this high release relates to an oxidized fraction from which the radionuclides are rapidly released. A high concentration of ~1E-4 M U is maintained, and, since the increase in concentration due to ongoing radiolytic oxidation appears to be about one order of magnitude less, this increase - if there is one – would not easily be detected.

The concentrations found for U and Pu in ampoules with old fragments are relatively high, triggering questions regarding potential solubility limits and colloid formation. As the samples are ultracentrifuged before analyses most potential colloids should have been removed. An assessment of solubility limits has been made using Spana (Puigdomenech et al., 2014) and data from the NEA-TDB (Grenthe et al., 2020). These calculations show that neither schoepite nor uranyl carbonate are expected to form in our systems. Regarding Pu, the radiolytic oxygen in the system is probably enough to allow Pu(V) in solution, and since this has a higher solubility than Pu(IV) this partly explains the high concentrations (Neck et al., 2007). It is also possible that this Pu(V) is in equilibrium with tiny colloidal particles not eliminated by the ultracentrifugation. Some remnant effect of colloids in the ampoules with old fragments is thus possible.

It is understandable that the old fragments, being subjected to part washing and part air humidity in the hot cell for at least 13 years, would have an oxidized layer that affects the results. It is less clear why the previous data (Cera et al., 2006) indicate a similar release of pre-oxidized material. If one assumes that the fragments used by Cera et al. (2006) were prepared around 2003, at the start of their project, those fragments should not have experienced a long oxidation time before the leaching started. The data of Cera et al. (2006) do not indicate any reduced yield of radiolytic gases but they do indicate a similar rapid increase of radionuclide concentrations. In any case, a pre-oxidized layer may have influenced the data of Cera et al. (2006), and this was indeed suggested by the authors since they observed that the calculated oxidative uranium dissolution underestimated the initial observed concentration. It is not clear from Cera et al. (2006) if the fragments were washed or pre-treated in any way before the leaching experiments started. One may speculate that if the fragments used by Cera et al. (2006) were stored in contact with air, solid state oxidation may have occurred but with no liquid water present, no secondary phase would have formed a surface layer. It may be that for the old fragments used in the current study, such a secondary layer was present, causing both a pulse release of pre-oxidized uranium and some shielding effect seen as lower yield of radiolytic gases.

Considering the complications found for the old fragments, the following discussion focuses on the new fragments. For the new fragments it is possible to observe an increase over time in the concentration for U, Pu, Sr, and Nd. This indicates that radiolytic oxidation is ongoing, causing a radionuclide release at rates that can be estimated using the fraction of the radionuclide inventory of the sample that is found in the aqueous phase, the so-called FIAP ("Fraction of Inventory in Aqueous Phase", Table 5). Dividing the FIAP by number of days and multiplying with 365, a yearly release rate can be estimated from the different ampoules (Fig. 7).

The higher fractional release of Cs & Tc compared with U, for new fragments, is not strange since it is well known that these elements are part of the so-called Instant Release Fraction (IRF), the non-matrix bound fraction. The data for iodine is not included in the fractional release discussion, since it is clear there is a risk of removing quite a significant fraction during the wash. For Cs, the washing of the new fragments did probably only remove a small part of the IRF. What is measured is therefore the part of the IRF still associated with the fragments, perhaps in grain boundaries. The measured rod average fission gas release (FGR) for this fuel was 2.4%. Previous studies indicate that the likely IRF for Cs is ca 1/3 of the FGR (Kienzler et al., 2017). In total therefore we would assume an IRF of Cs of ca 8E-3. The release measured in this study, on average 1.5E-3. There is no ICP-MS data from the wash of the new fragments, but based on the fraction of U released during the wash (on average ca 6E-8), and the ratio of FIAP for Cs and U in the leach solution (ca 13), one can estimate a Cs release during the wash on average only ca 8E-7 (13 x 6E-8). In total the estimated Cs release from wash and leaching is thus ca 1.5E-3 of the Cs inventory in the new fragments. This is less than the expected part of Cs IRF. The reason why no increase is observed over five years is probably that the IRF release, that happened already in the first year, dominates the release. A continued release based on oxidative dissolution of the spent fuel matrix assuming a dissolution rate of 1E-5 per year which is in line the U data, should have released ca 5E-5 of the Cs over five years. This is

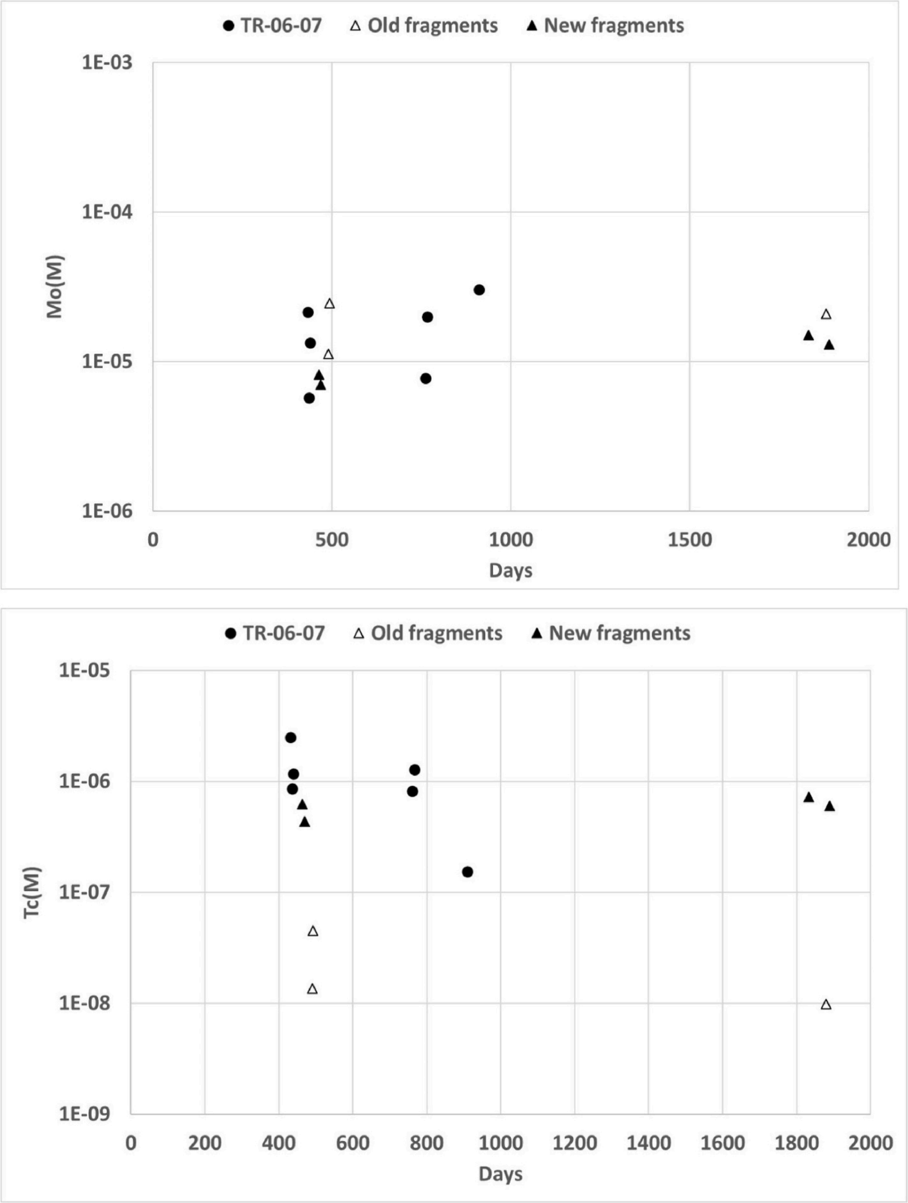

Fig. 6. Mo and Tc concentrations. TR-06-07: Data from Cera et al. (2006); Old fragments: Previously prepared samples; New fragments: Samples prepared for this study. Estimated analytical error for old and new fragments is ca 10% corresponding to the size of the data symbols.

Table 5
FIAP for different radionuclides in the ampoules with new fragments.

Ampoule	6	10	11	13
Days	471	475	1836	1880
Sr-90	4.2E-05	4.1E-05	8.4E-05	8.4E-05
Mo-100	4.1E-03	3.5E-03	4.0E-03	7.0E-03
Tc-99	1.5E-03	1.0E-03	1.4E-03	1.4E-03
Cs-133	1.8E-03	1.6E-03	1.8E-03	8.2E-04
La-139	1.4E-06	1.3E-06	1.4E-06	2.0E-06
Nd-144	1.1E-06	1.0E-06	1.1E-06	1.7E-06
U-238	6.2E-05	4.1E-05	6.1E-05	2.9E-04
Np-237	5.6E-06	3.0E-06	5.5E-06	1.9E-05
Pu-239	5.2E-07	5.9E-07	5.1E-07	3.3E-06

only ca 3% of the total Cs released. Thus, no increase over time due to matrix dissolution is discerned.

For Tc in the ampoules reported here (fresh fragments), the data indicate a leached fraction between 1E-3 and 1.5 E−3. The estimated washed out fraction of Tc is only ca 7E-7. For Mo, the FIAP is between 3E-3 and 7E-3. The released fractions of Tc and Mo is thus in line with what was reported by Kienzler et al. (2017). Both Tc and Mo are expected to be released from the fuel as oxidized anions, and at least part of Mo is expected to be oxidized in the reactor and thereby buffer the oxygen potential. One might speculate that a high burnup fuel would display a higher FIAP of these elements compared with a fuel with lower burnup.

The U-238 & Sr-90 release rates (Fig. 7) are ~1–3 E−5 FIAP per year, in line with what was observed by Forsyth (1997) for similar conditions. Since measured U concentrations of up to ca 3E-5 M clearly is above the solubility of UO_2 (~3E-9 M, Neck and Kim, 2001), the U in the aqueous solution is oxidized and a result of radiolytic oxidation. Looking at Cs-133 the release rates are higher, but this is not expected to be related to matrix oxidation; this release is expected to be coming from the IRF. Regarding Tc-99, Kienzler et al. (2017) observed a long term release rate of ca 1E-5 FIAP per day (3.65E-3 per year); in the current study, the apparent annual release rate of Tc is, on average, ca 6E-4.

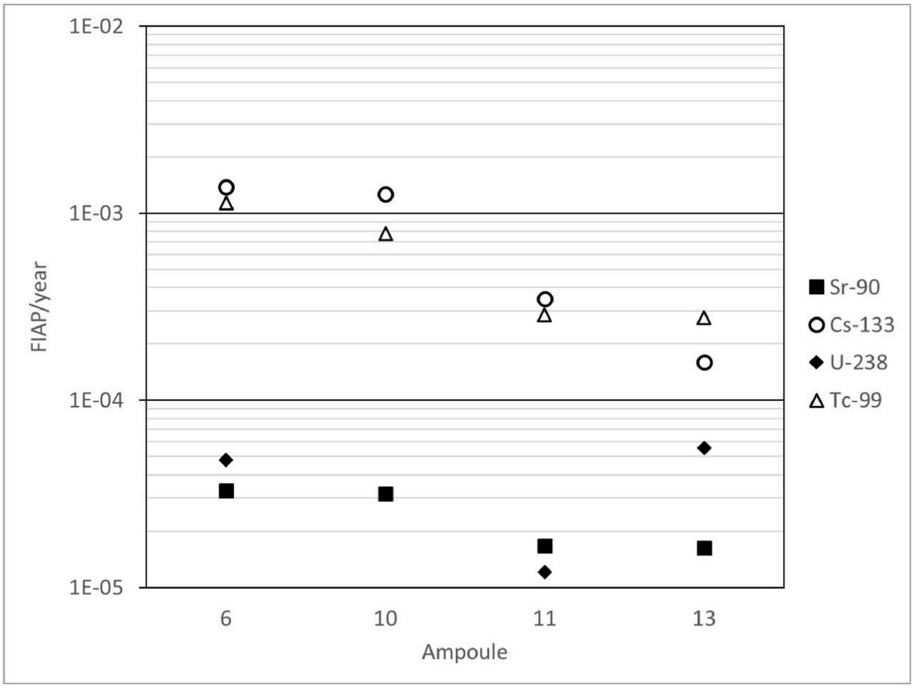

Fig. 7. FIAP/year for ampoules 6,10,11 and 13 with new fragments.

5. Conclusions

In the current study, a set of ampoules produced in a similar fashion as a previous study (Cera et al., 2006), were opened and analysed. The purpose was to continue the data series to provide data up to ca five years. Fragments from the same fuel was used and the fluid and gas compositions were the same as the relevant set of the Cera et al. (2006) experiments.

The first observation is that the history of the spent fuel fragments plays an important role in the results. Already during experiment set-up, it became clear that old fragments, prepared for the previous study (Cera et al., 2006), had been oxidized and required an extensive wash period in order to reduce the amount of already oxidized uranium on the surface of the fragments. Other, newly crushed fragments, that were taken from the same fuel rod for this experiment, did not display this behaviour. Thus, the data collected from the ampoules sealed in 2016 and reported here, belong to two groups: old fragments and new fragments.

The radiolytic O_2 and H_2 gases showed no or very limited increase between one and five years. This is a similar trend as previously observed by Cera et al. (2006). In the ampoules with old fragments, it appears less radiolytic gases have collected. A difference in leaching behaviour is also observed between old and new fragments. New fragments have released significantly less actinides and fission products than the old fragments. The release from old fragments is similar to that observed by Cera et al. (2006), meaning that high concentrations (~1E-4 M U), are reached after ca one year, after which no clear concentration increase is observed.

For new fragments, radionuclide concentrations are one or more orders of magnitude lower than for old fragments. This is likely due to much lower release of pre-oxidized material. For these ampoules, a continued release of radionuclides (except Cs and possibly I) over five years is observed. Notably, Cs concentrations do not increase. This leaching behaviour indicates that the so-called instant release fraction dominates the released fraction and any additional release from continued matrix oxidation is too small to be observed. The release of Tc and Mo are found to be similar to what has observed previously (Cera et al., 2006; Kienzler et al., 2017).

The data presented here show that with careful sample selection and preparation, radiolytically induced oxidative dissolution of spent fuel can be observed for up to five years in a closed, initially anoxic system. The apparent fuel dissolution rate, based on fractions of inventory releases, is estimated to between 2E-5 and 3E-5 per year, based on release of Sr-90 and U-238.

CRediT authorship contribution statement

Lena Z Evins: Writing – original draft, Conceptualization. **Charlotta Askeljung:** Writing – review & editing, Methodology, Investigation. **Alexandre Barreiro Fidalgo:** Writing – review & editing, Methodology, Investigation. **Anders Puranen:** Writing – review & editing, Investigation. **Olivia Roth:** Writing – review & editing. **Kastriot Spahiu:** Writing – review & editing, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors would like to thank the staff at the hot cell laboratory at Studsvik Nuclear AB. This research was financed by the Swedish Nuclear Fuel and Waste Management Company (SKB).

Data availability

Data will be made available on request.

References

Bauhn, L., Hansson, N., Ekberg, C., Fors, P., Delville, R., Spahiu, K., 2018a. The interaction of molecular hydrogen with α-radiolytic oxidants on a $(U,Pu)O_2$ surface. J. Nucl. Mater. 505, 54–61.

Bauhn, L., Ekberg, C., Fors, P., Spahiu, K., 2018b. The fate of hydroxyl radicals produced during H_2O_2 decomposition on the SIMFUEL surface in the presence of dissolved hydrogen. J. Nucl. Mater. 507, 38–43.

Broczkowski, M., Zagidulin, D., Shoesmith, D.W., 2010. The role of dissolved hydrogen on the corrosion/dissolution of spent nuclear fuel. In: Nuclear Energy and the Environment, vol. 1046. ACS Symposium Proceedings, pp. 349–380. Chapter 26.

Bruno, J., Cera, E., Grivé, M., Eklund, U.-B., Eriksen, T., 1999. Experimental Determination and Chemical Modelling of Radiolytic Processes at the Spent Fuel/water Interface, SKB TR-9vols. 9–26. Svensk Kärnbränslehantering AB.

Burkholder, J.B., Sander, S.P., Abbatt, J.P.D., Barker, J.R., Cappa, C., Crounse, J.D., Dibble, T.S., Huie, R.E., Kolb, C.E., Kurylo, M.J., Orkin, V.L., 2019. Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation No. 19. JPL Publication 19-5. Jet Propulsion Laboratory. https://jpldataeval.jpl.nasa.gov.

Carbol, P., Fors, P., Gouder, T., Spahiu, K., 2009. Hydrogen suppresses UO_2 corrosion. Geochem. Cosmochim. Acta 73 (15), 4366–4375.

Cera, E., Bruno, J., Duro, L., Eriksen, T., 2006. Experimental determination and chemical modelling of radiolytic processes at the spent fuel/water interface. Long Contact Time Experiments SKB-TR-06-07. Swedish Nuclear Fuel and Waste Management Co.

Ekeroth, E., Granfors, M., Schild, D., Spahiu, K., 2020. The effect of temperature and fuel surface area on spent nuclear fuel dissolution kinetics under H_2 atmosphere. J. Nucl. Mater. 531, 151981.

Eriksen, T.E., Jonsson, M., Merino, J., 2008. Modelling of time resolved and long contact time dissolution studies of spent nuclear fuel in 10 mM carbonate solution–a comparison between two different models and experimental data. J. Nucl. Mater. 375 (3), 331–339.

Forsyth, R., 1997. The SKB Spent Fuel Corrosion Programme. An Evaluation of Results from the Experimental Programme Performed in the Studsvik Hot Cell Laboratory. SKB TR 97-25. Svensk Kärnbränslehantering AB.

Grenthe, I., Gaona, X., Rao, L., Plyasunov, A., Runde, W., Grambow, B., Konings, R., Smith, A., Moore, E., Ragoussi, M.E., Martinez, J.S., 2020. Second update on the chemical thermodynamics of uranium, neptunium, plutonium, americium and technetium. In: Chemical Thermodynamics, vol. 14. Organisation for Economic Co-Operation and Development. No. NEA–7500.

Hansson, N.L., Jonsson, M., 2023. Exploring H2-effects on radiation-induced oxidative dissolution of UO2-based spent nuclear fuel using numerical simulations. Radiation Physics and Chemistry 210, 111055.

Icenhour, A.S., Toth, L.M., Wham, R.M., Brunson, R.R., 2004. A simple kinetic model for the alpha radiolysis of water sorbed on NpO_2. Nuclear technology 146 (2), 206–209.

Jonsson, M., 2022. Assessment of homogeneous processes and parameters to be used in models for radiation induced dissolution of spent nuclear fuel. SKB R-22-06, Svenska Kärnbränslehantering AB.

Jonsson, M., 2023. Assessment of heterogeneous processes and parameters to be used in models for radiation induced dissolution of spent nuclear fuel. In: SKB R-22-06. Svenska Kärnbränslehantering AB.

Jonsson, M., Nielsen, F., Roth, O., Ekeroth, E., Nilsson, S., Hossain, M.M., 2007. Radiation induced spent nuclear fuel dissolution under deep repository conditions. Environmental science & technology 41 (20), 7087–7093.

Kienzler, B., Duro, L., Lemmens, K., Metz, V., De Pablo, J., Valls, A., Wegen, D.H., Johnson, L., Spahiu, K., 2017. Summary of the Euratom Collaborative project FIRST-Nuclides and conclusions for the Safety case. Nucl. Technol. 198 (3), 260–276.

Neck, V., Kim, J.I., 2001. Solubility and hydrolysis of tetravalent actinides. Radiochim. Acta 89 (1), 1–16.

Neck, V., Altmaier, M., Seibert, A., Yun, J.I., Marquardt, C.M., Fanghänel, T., 2007. Solubility and redox reactions of Pu (IV) hydrous oxide: Evidence for the formation of PuO2+ x (s, hyd). Radiochim. Acta 95 (4), 193–207.

Nilsson, S., Jonsson, M., 2011. H_2O_2 and radiation induced dissolution of UO2 and SIMFUEL pellets. J. Nucl. Mater. 410, 89–93.

Puigdomenech, I., Colàs, E., Grivé, M., Campos, I., Garcia, D., 2014. A tool to draw chemical equilibrium diagrams using SIT: Applications to geochemical systems and radionucldie solubility. MRS Symp Proc Vol 1665, Scientific Basis for Nuclear Waste Management. DOI: 10:1557/opl.2014.635.

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

Puranen, A., Barreiro, A., Evins, L.Z., Spahiu, K., 2020. Spent fuel corrosion and the impact of iron corrosion–The effects of hydrogen generation and formation of iron corrosion products. J. Nucl. Mater. 542, 152423.

Spahiu, K., Cui, D., Lundström, M., 2004. The fate of radiolytic oxidants during spent fuel leaching in the presence of dissolved near field hydrogen. Radiochim. Acta 92, 625–629.

Trummer, M., Jonsson, M., 2010. Resolving the H_2 effect on radiation induced dissolution of UO2-based spent fuel. J. Nucl. Mater. 396, 163–169.

Young, C.L., 1981. IUPAC Solubility Data Series: Vol. 5/6. Hydrogen and Deuterium. Pergamon Press, Oxford. ISBN 0080239277.

Zakova, J., 2018. Inventarieberäkningar för bränslelakningsförsök. Studsvik Technical Note – SC-18-052. Internal Report.