

LEACHING OF HIGH BURN-UP UO_2 AND MOX FUEL RODS WITH PRE-SET CLADDING DEFECTS

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ABSTRACT

In order to simulate the realistic case of groundwater coming into contact with a spent nuclear fuel repository, the leaching of irradiated MOX (12, 20 and 25 GWd/tU) and UO_2 (30 and 50 GWd/tU) fuel rods with pre-set cladding defects has been studied. Leaching experiments in de-ionised water at 100°C under anoxic or reducing conditions were performed. The release of the main radionuclides (uranium, plutonium, strontium and caesium) can be described by considering a two-step dissolution mechanism that includes the initial dissolution of an oxidised layer present on the fuel surface and a long-term oxidative matrix dissolution. No significant differences between MOX and UO_2 fuels were found for uranium release, but for plutonium and fission products the release was about two orders of magnitude higher for MOX fuels compared to UO_2 . Especially high initial release rates for caesium and iodine were found probably due to the migration of these volatile radionuclides upon irradiation to the pellet rim, i.e. the surface in contact with the groundwater. Long-term dissolution rates were calculated for the major fuel constituents and fission products and the values obtained are approximately representative of the fuel matrix dissolution.

INTRODUCTION

It is generally accepted that the processes by which radionuclides originated from a spent fuel waste repository will be released, are dissolution and transport as a result of the groundwater flow (1). The cladding will be the last barrier before the water comes into contact with the fuel, namely with the outer RIM of the pellet. The release of the actinide elements including the matrix elements uranium and plutonium will be limited by the low solubility product of the actinide-bearing solids and the flow rate of the water through the waste package (2,3). On the other hand, the release of highly soluble radionuclides like caesium and iodine may depend both

- on the heterogeneous distribution of these radionuclides within the fuel as a consequence of migration to the grain boundaries (together with other fission products) and to the pellet periphery (together with fission gases) and
- on the durability of the fuel matrix in a potential repository.

It is generally agreed (4) that the dissolution of soluble radionuclides from spent fuel can be divided into components that come from three different areas:

- 1) The fuel/cladding gap, including the spaces between fuel pellets and the open porosity and cracks within the pellets.
- 2) The grain boundaries of the fuel pellets.
- 3) The UO_2 matrix.

If groundwater penetrates inside of the fuel rod through a defect, S/V ratios are rather high and the relative importance of α -radiolysis in the overall radiolysis process is increased due to an increased

inventory of α -emitters in the outer pellet zone as a consequence of increased epithermal neutron capture during irradiation.

In order to study all these effects, different spent fuel rodlets (including MOX and UO₂ fuels with varying burn-up) with preset defects on the cladding, were leached in the present study.

EXPERIMENTAL

Three MOX fuel (12, 20 and 25 GWd/tU) and three UO₂ fuel (one with 30 and two with 50 GWd/tU) rodlets, each of them about 6 cm long, were used. Both ends of each sample were closed by means of tight stainless steel end-caps. One UO₂ fuel rod with a burn-up of 50 GWd/tU was provided with two series of defects (in each case, 3 holes of 1 mm diameter each), one series at the top and in contact with vapour and the other at the bottom of the rodlet and in contact with the leaching solution. In all the other samples, the defects were placed in the centre of the rodlet and the autoclave was filled completely with the leaching solution.

MOX fuels were fabricated following the MIMAS (MICronized-MAStEr) blend process with Pu-rich aggregates (19 μ m and 20 % plutonium) in a natural UO₂ matrix (grain size 5 μ m). The average plutonium content of the fuel matrix is 6.9 %.

The leaching was carried out in autoclaves equipped with Ti-liners using deionized water at 100°C under anoxic or reducing conditions. Large metal surfaces, i.e. titanium (autoclave liners), zircaloy (cladding) and stainless steel (end-caps) could be efficient scavengers of oxidising species.

The released amounts of radionuclides were measured by ICP-MS

RESULTS AND DISCUSSION

Release Rates

Figure 1 shows the evolution of the amount of uranium, plutonium, caesium and strontium released in solution with time for MOX (25 GWd/tU) and UO₂ (50 GWd/tU) fuels. The behaviour is very similar in both fuels, with an initial fast dissolution followed by a much slower long-term dissolution. Iodine shows a slightly different behaviour, i.e. after a fast initial dissolution there is a second increase of the iodine concentration in solution (up to 50 days) before the slow dissolution rate is observed.

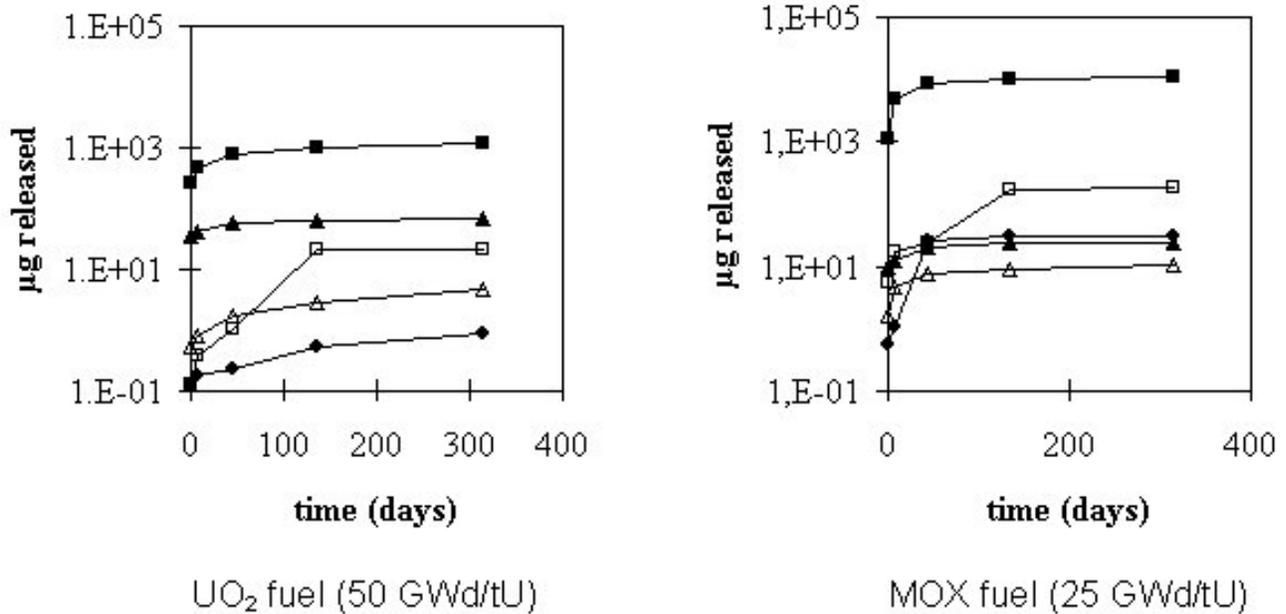


Figure 1. Cumulative release of the different radionuclides studied (in µg) for both types of fuel. ■ caesium, ▲uranium, □ iodine, △strontium and ● plutonium.

Except for uranium, the release is higher in the case of MOX fuels, one order of magnitude for fission products and almost two for plutonium, despite a burn-up which is only half that of UO₂.

Dissolution Mechanism, Application of a Dissolution Model

A dissolution model developed for unirradiated UO₂ (5) was applied to the present results. This model assumes that the fast initial dissolution is due to the presence of an oxidised layer on the UO₂ surface (6) and the second step is due to an oxidative dissolution of UO₂.

The process can be described with the following equation, assuming an initial uranium concentration in solution equal to zero:

$$[U] = [U]_f - [U]_0 + [U]_0(1 - \exp(-k_1t)) + ([U]_0 - [U]_f)\exp(-k_2t) \quad (\text{Eq. 1})$$

where k_1 and k_2 are the rate constants (s^{-1}) of the initial and long-term dissolution, respectively, $[U]_0$ is the solubility of the oxidized layer present initially on the UO₂ surface (mol kg^{-1}), $[U]_f$ (mol kg^{-1}) is the solubility of the thermodynamically stable solid phase under these conditions $[U]$ is the uranium concentration in solution (mol kg^{-1}) and t is the time (s).

Figure 2 shows that the fit of the model to the results of uranium concentration in solution is very good for all six fuel samples.

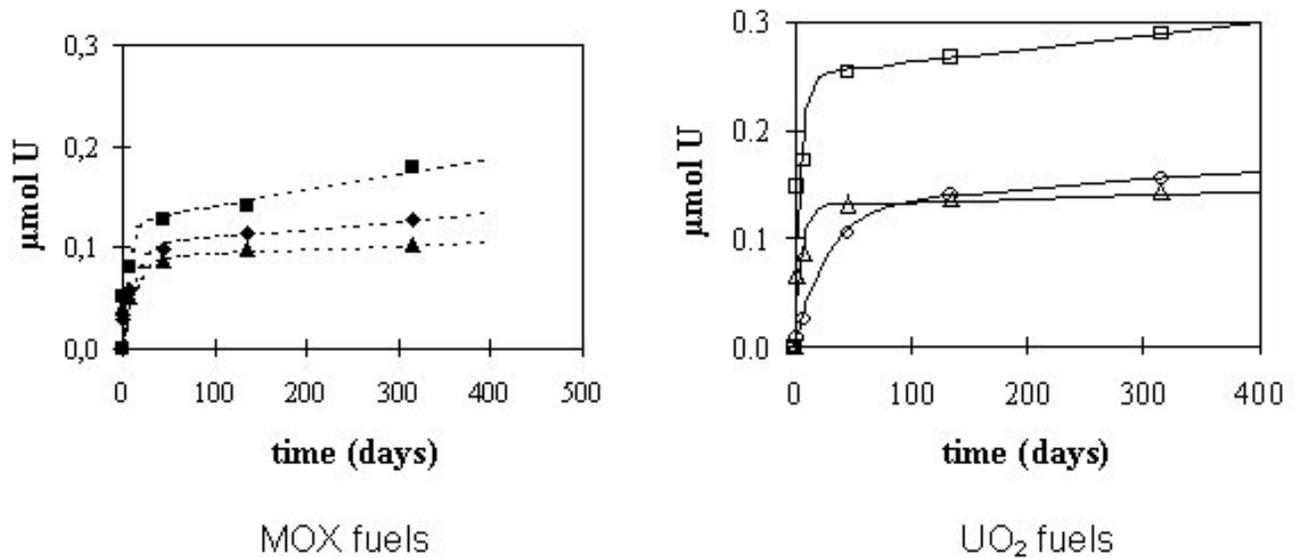


Figure 2. Fitting of the model to the experimental data for uranium release from the different fuels. ▲MOX fuel (12 GWd/tU), ◆MOX fuel (20 GWd/tU), ■ MOX fuel (25 GWd/tU), △ UO₂ fuel (30 GWd/tU), o UO₂ fuel (50 GWd/tU) and UO₂ fuel (50 GWd/tU with two series of defects). The lines represent the model.

A similar good fit was obtained for plutonium, caesium and strontium, indicating that these elements follow the dissolution process of UO₂ as described above.

Fraction of Inventory in the Aqueous Phase (FIAP)

FIAP values were calculated using account the specific elemental mass inventory of the fuels obtained by means of the ORIGEN code (7). The values obtained for uranium are shown in Fig. 3.

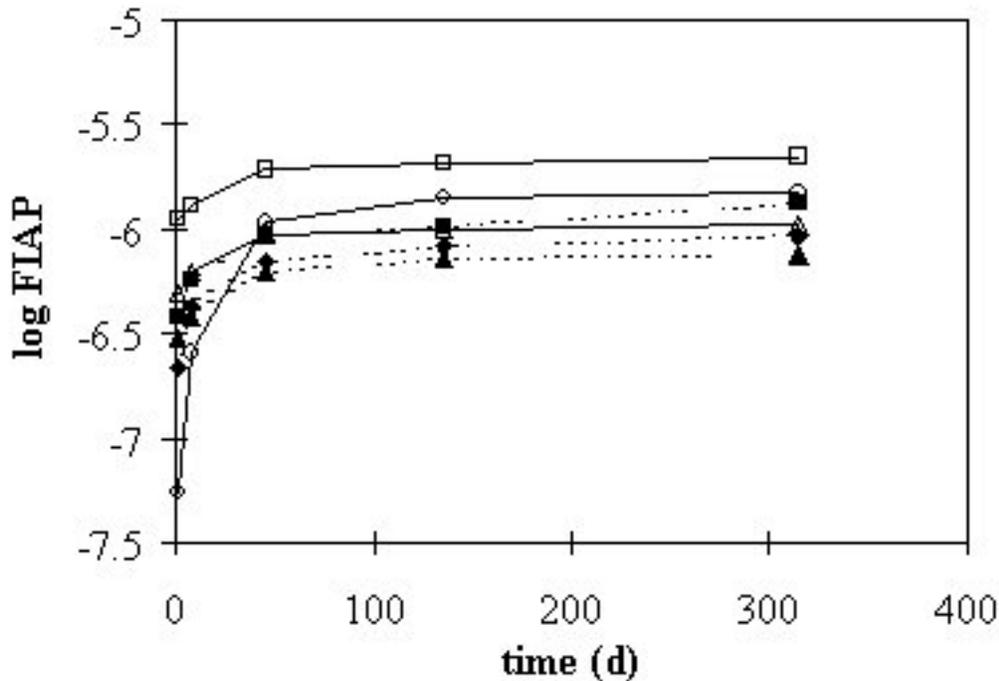


Figure 3. FIAP values for uranium.

▲MOX fuel (12 GWd/tU), ◆MOX fuel (20 GWd/tU), ■ MOX fuel (25 GWd/tU), △ UO₂ fuel (30 GWd/tU), ○ UO₂ fuel (50 GWd/tU) and ◻ UO₂ fuel (50 GWd/tU with two series of defects).

The FIAP values after 315 days are quite similar for all the fuels and almost independent on the burn-up and type of fuel. The slightly higher FIAP value for the high burn-up UO₂ is probably due to a higher initial dissolution of oxidised UO₂ and could be related to a higher inventory of α-emitters in the rim zone produced by epithermal neutron capture. The increased radiation dose could have led to an increased oxidation of the surface. On the other hand, in the case of all the other radionuclides the FIAP values are always about two orders of magnitude higher for MOX than for UO₂ fuels, as can be seen in the results presented in Table I.

Table I. FIAP values at 315 days.

	MOX 12	MOX 20	MOX 25	UO ₂ 30	UO ₂ 50	UO ₂ 50*
uranium	9.38 10 ⁻⁷	1.30 10 ⁻⁶	7.58 10 ⁻⁷	1.05 10 ⁻⁶	2.18 10 ⁻⁶	1.50 10 ⁻⁶
plutonium	4.17 10 ⁻⁶	1.03 10 ⁻⁴	3.14 10 ⁻⁵	2.24 10 ⁻⁶	2.76 10 ⁻⁶	2.31 10 ⁻⁷
strontium	3.48 10 ⁻⁴	4.23 10 ⁻⁴	4.20 10 ⁻⁴	1.30 10 ⁻⁴	1.34 10 ⁻⁴	8.35 10 ⁻⁵
caesium	0.129	0.165	0.147	3.97 10 ⁻³	1.02 10 ⁻²	4.25 10 ⁻³
iodine	9.38 10 ⁻³	1.22 10 ⁻²	2.56 10 ⁻²	6.18 10 ⁻⁴	1.66 10 ⁻³	1.55 10 ⁻⁴

* Experiment with two series of defects.

These values are in good agreement with literature data in similar experiments on UO₂ fuel rods by Wilson and Oversby (8) and on CANDU UO₂ by Stroes-Gascoyne et al. (9). For the differences observed between UO₂ and MOX several explanations are possible:

- a lower burn-up of MOX and consequently a larger gap between fuel and cladding, i.e. a larger surface in contact with water
- the special structure of MOX with agglomerates containing originally 20 % of plutonium (fissile material) incorporated in natural UO₂ upon irradiation. This structure leads to :
 - a concentration of fission events in the agglomerates (>200 GWd/tU) and release of volatile fission products (caesium, iodine).
 - a strong neutron capture by depleted uranium in the outer periphery, leading to an increased inventory of fission products and plutonium.

Comparison with results obtained by Serrano et al. (10) on particles from the centre of fuel pellet shows a significantly higher release of caesium, strontium and plutonium for both MOX and UO₂ fuels in our experiments. This difference can again be attributed to the higher inventory of these elements in the RIM zone (11,12).

Especially the high plutonium release could also be due to galvanic effect, which could increase the dissolution of the two-phase material (13).

Long-Term Oxidative Dissolution

The long-term oxidative dissolution rates, normalized to the surface area, were calculated using the model mentioned above. For this normalization the specific surface area measured by the BET method for pellets of unirradiated uranium dioxide (14) was used, i.e. $1.9 \cdot 10^{-4} \text{ m}^2\text{g}^{-1}$. It can be considered that this is a conservative value, assuming that spent fuel has a much higher surface area at the fuel-pellet interface due to the formation of a highly porous micrograin structure (15).

The values obtained which represent the long-term oxidative dissolution are presented in Table II.

Table II. Dissolution rates (in $\text{mg m}^{-2} \text{ d}^{-1}$) calculated using the dissolution model.

	MOX 12	MOX 20	MOX 25	UO ₂ 30	UO ₂ 50
Uranium	$2.61 \cdot 10^{-3}$	$5.56 \cdot 10^{-3}$	$1.22 \cdot 10^{-3}$	$1.04 \cdot 10^{-3}$	$4.17 \cdot 10^{-3}$
Plutonium	$1.77 \cdot 10^{-3}$	$5.30 \cdot 10^{-3}$	$8.83 \cdot 10^{-4}$	$2.19 \cdot 10^{-4}$	$3.53 \cdot 10^{-4}$
Strontium	$2.56 \cdot 10^{-3}$	$7.02 \cdot 10^{-4}$	$1.34 \cdot 10^{-3}$	$8.30 \cdot 10^{-4}$	$1.66 \cdot 10^{-3}$
Caesium	$7.11 \cdot 10^{-2}$	$2.60 \cdot 10^{-3}$	$6.51 \cdot 10^{-3}$	$3.24 \cdot 10^{-2}$	$1.19 \cdot 10^{-1}$

As expected, the dissolution rates for uranium and strontium are quite similar for both types of fuel. Plutonium values are always the lowest ones, similar to samples originated from the pellet center (10). On the contrary, for caesium dissolution rates are still higher, especially for the high burn-up UO₂, this can be explained by an increased inventory of caesium in the gap due to its radial migration upon irradiation (increasing with burn-up).

CONCLUSIONS

The present study on defect UO₂ and MOX fuel rods simulating the case of groundwater intrusion into the fuel pin in case of cladding failure, shows that the dissolution process can be described by a two-step dissolution model with a fast initial dissolution of an oxidised layer on the pellet surface followed by oxidative matrix dissolution.

The FIAP values representing the fast initial dissolution show that the uranium release is almost the same for UO₂ and MOX fuels, and for both fuels the release of plutonium and fission products is higher compared to uranium. Higher release rates in MOX fuels compared to UO₂ fuels are due to the special two phase structure of MOX fuel, leading to an increased inventory at the pellet periphery, i.e. the surface in contact with the leachant. Especially high FIAP values were found for caesium and iodine, due to a migration of these radionuclides to the RIM zone of the pellet upon irradiation.

The long-term dissolution rates are similar for uranium, plutonium and strontium in MOX fuels seemingly independent on the burn-up of the fuel. In the case of UO₂ fuels these dissolution rates seem to increase slightly with burn-up, and plutonium always has the lowest values.

Detailed examination of the leached samples by EPMA, optical and electron microscopy should help to better understand ongoing processes during the dissolution process including the definition of the surface in contact with water or the formation of secondary phases during the leaching process.

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