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# Influence of low temperature air oxidation on the dissolution behaviour of $UO_2$ and MOX spent fuel

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## Abstract

The dissolution behaviour of pre-oxidised LWR $UO_2$ and MOX spent fuel was studied by means of semi-dynamic leaching tests. The fuels, irradiated to burn-ups of 53 and 39 GWd $t^{-1}$ respectively, were thermally treated at 250°C in air for various times, up to different oxygen/metal (O/M) ratios. The leaching tests performed in deionised water at ambient temperature revealed, for both $UO_2$ and MOX, an instantaneous release strongly dependent on the oxidation degree. After this initial stage, a very low leaching rate, almost independent of the O/M-ratio, was measured. For both fuel types, the fission products considered showed a fractional release normalised to that of uranium higher than 1, due to either the larger inventory at grain boundaries as a consequence of migration upon irradiation or to the inherent higher solubility of some of these elements. In contrast to fission products, the fractional release of Pu from the $UO_2$ fuel was not affected by the oxidation level of the fuel and was one order of magnitude lower than the release of U. For MOX fuel, the intrinsic heterogeneity of the material due to Pu as fissile element being concentrated in agglomerates, led to a stronger release of this element relative to the U-matrix for the non-oxidised sample. After oxidation, which affects almost exclusively the matrix, the instantaneous release rate of Pu is again significantly lower in comparison to U. © 1998 Elsevier Science S.A.

*Keywords:* Leaching; Oxidation; Spent fuel; LWR $UO_2$ fuel; LWR MOX fuel; Uranium; Plutonium; Fission products

## 1. Introduction

The direct disposal of spent fuel as waste form is currently under consideration in many countries. The repository sites explored are often above the water table and thereby relatively dry. A failure of the waste package would expose the fuel to an air atmosphere and consequently lead to its partial oxidation. At a later stage, this more or less oxidised fuel could come in contact with underground water. In order to compare the behaviour of different types of fuel under these conditions, the present study was initiated to investigate the influence of the oxidation state on the dissolution behaviour of high burn-up LWR $UO_2$ and MOX spent fuels. From the point of view of final disposal MOX fuels little information is available, although their significantly higher susceptibility towards oxidation is well established [1]. In fact, MOX fuels, having a duplex structure with Pu rich agglomerates (up to 200 μm in size) distributed in a matrix of natural $UO_2$, are found to oxidise to $U_3O_8$ instead to $U_4O_{9+x}$ [1] which is the transformation phase of spent $UO_2$ fuels upon oxidation [2,3]. This difference in the oxidation behaviour should have an influence on radionuclide release into a leachant.

## 2. Experimental conditions

Specimen fragments of about 0.3 g, were taken from the central part of LWR $UO_2$ and MOX spent fuel pellets irradiated to burn-ups of 53 and 39 GWd $t^{-1}$ respectively. The MOX fuel was fabricated by mechanically blending a mix of 70/30 $UO_2/PuO_2$ with natural $UO_2$, the percentage occupied by the MOX agglomerates (about 50 μm in size) being around 15 vol % of the fuel [4]. The fragments were annealed at 250°C in air for various durations up to 120 days [1]. The O/M ratios calculated assuming that all the weight change is due to the oxygen reaction with uranium are shown in Table 1.

Table 1
Change in O/M ratio of the specimens during annealing tests

| Oxidation time | 0 | 10 days | 30 days | 120 days |
|---|---|---|---|---|
| $UO_2$ | 2.0 | 2.35 | 2.39 | 2.44 |
| MOX | 2.0 | 2.34 | – | 2.53 |

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The oxidised fuel fragments were leached in a sequential mode at ambient temperature in 20 ml of deionised water for test durations between 24 and 750 h. The leaching tests were performed as follows: Fuel specimens were immersed in water and the vessels were kept closed during each run. After completion of each contact period, the specimens were transferred to a new vessel with fresh leachant. The empty vessels were rinsed with 1 M $HNO_3$. The chemical analyses of the leachants and rinse solutions were performed by ICP–MS (ELAN 5000, Perkin Elmer Sciex).

Assuming an ideal spherical form, the geometric area of the sample gave a calculated surface/volume ratio of approximately 2 $m^{-1}$.

## 3. Results and discussion

The leaching results obtained for the main fission products and actinides are represented as a fraction of inventory, i.e. the ratio between the amount measured in the leachant and the content of the corresponding element in the fuel, obtained from KORIGEN code calculations. The cumulative fractional release (sum of all previous chronological values) of U from $UO_2$ and MOX specimens at different O/M ratios is represented in Fig. 1.

As expected, for both types of fuel the initial fractional release is higher when the O/M ratio increases due to the presence of increasing amounts of soluble U(VI) at the surface of the fuel particle. An additional contribution probably comes from less dense U phases formed during the oxidation treatment, leading to a higher surface area exposed to the water attack. However, this effect is strictly limited to the first instantaneous release represented by the first measurement after 24 h. Subsequent leaching steps were not affected by the oxidation degree of the fuel and showed very low leaching rates ($3.10^{-7}$ g $cm^{-2}$ $day^{-1}$ for $UO_2$ and $2.10^{-7}$ g $cm^{-2}$ $day^{-1}$ for MOX fuel) independent from the oxidation degree of the fuel.

Comparing the non-oxidised samples (Fig. 1), the U fractional release of $UO_2$ fuel is about one order of magnitude higher than for the MOX fuel. This strong difference is related to the differences in the microstructure discussed above. In fact, in MOX fuel fission events are of course mainly concentrated to the Pu-agglomerates and leave the U- matrix, i.e. most of the surface exposed to the leachant, practically unchanged. For $UO_2$, on the contrary, the fission events and the related surface changes are homogeneously distributed over the total surface of the fuel particle.

The situation changes for the oxidised fuel samples (Fig. 1). For $UO_2$ the U release rate increases by about half an order of magnitude and for MOX fuel by more than two orders of magnitude. This result can be explained by the fact [5], that MOX fuels present a higher bias to oxidation at low temperatures than irradiated $UO_2$ fuels. This higher U(VI) content and also the physical degradation due to the formation of a less dense phase leads to a higher fractional release and explain the values obtained.

The fractional release normalised to U for the main fission products and for Pu normalised to U from $UO_2$ and MOX fuels is shown in Fig. 2 and Fig. 3, respectively. A comparison is made between the non-oxidised specimen and the one with the highest oxidation degree (Table 1). For all four samples, the fission products showed a higher fractional release than U. This has been attributed in some cases to the migration of the fission products to the grain boundaries upon irradiation which become weaker after the oxidation treatment or, in the case of non-oxidised samples, to the inherent higher solubility of some elements.

The difference between the fission products and U fractional release is reduced for the oxidised sample, especially in the case of MOX (cf., explanation given above). The exception is Tc due to its known intrinsic

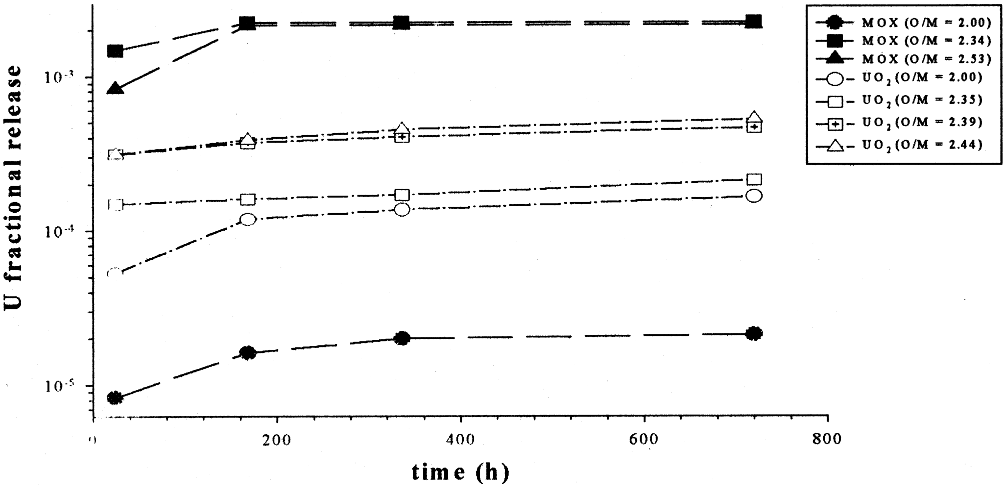

Fig. 1. Cumulative fractional release for U from $UO_2$ and MOX fuel specimens as a function of contact time.

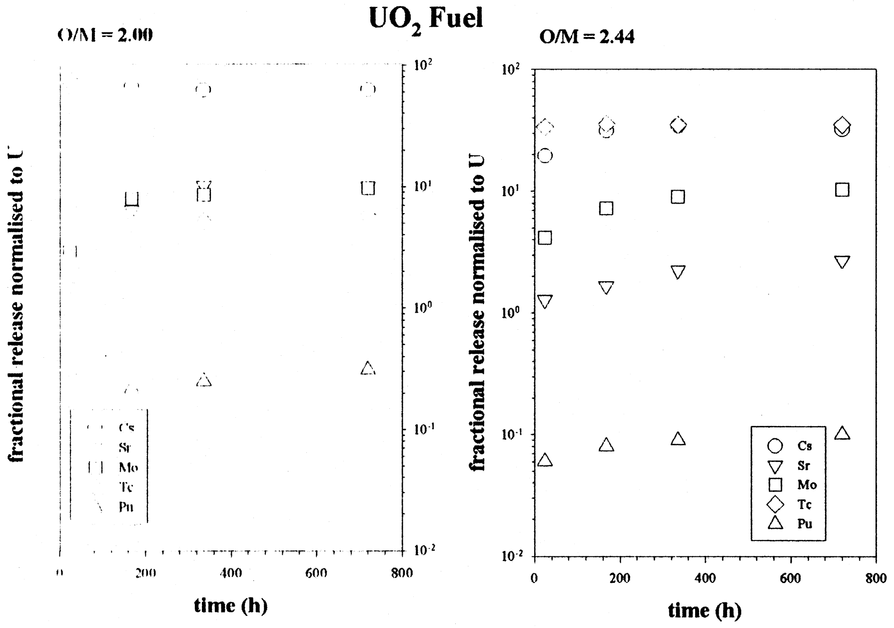

Fig. 2. Influence of fuel O/M ratio on the fractional release normalised to U of several fission products and Pu from $UO_2$ fuel.

redox sensitivity. The oxidation has led to extensive oxidation of Tc present at the grain boundaries to the highly soluble $TcO_4^-$.

For Pu the normalised fractional release is lower than that of U with the exception of the non-oxidised MOX sample where, as shown above, the U release rate is very low. The normalisation to the total U leads to this relatively high Pu release value.

## 4. Conclusions

Oxidation at low temperature of both MOX and $UO_2$ fuels leads to a higher fractional release at the initial leaching stage. The subsequent dissolution rates are very low ($2–3\times10^{-7}$ g $cm^{-2}$ $day^{-1}$) and almost not affected by pre-oxidation of the fuel.

The special structure of MOX fuel with Pu agglomerates

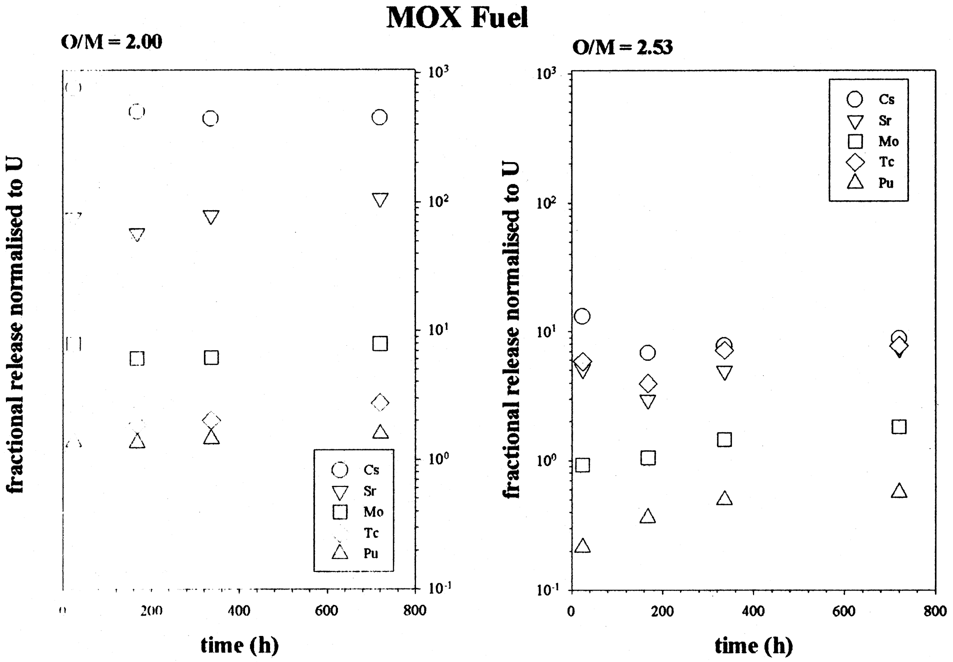

Fig. 3. Influence of fuel O/M ratio on the fractional release normalised to U of several fission products and Pu from MOX fuel.

incorporated in a matrix of natural $UO_2$ leads to increased sensitivity towards oxidation and as a consequence to a higher fractional release of U compared with $UO_2$. For dissolution studies MOX can be considered as a two-phase material with Pu and fission products mainly contained in agglomerates.

The Pu amount released from the $UO_2$-fuel is low and not affected by the oxidation level of the fuel.

In both cases, $UO_2$ and MOX, the fission products show a higher fractional release as compared with uranium, due to their migration to the grain boundaries upon fuel irradiation. With the exception of Tc, which is oxidised to the highly soluble $TcO_4^-$, oxidation of the fuel leads to an increased U release especially for MOX fuels leading to a relative decrease of the fission product fractional release,

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