Journal of Nuclear Materials 294 (2001) 339–343

journal of nuclear materials

www.elsevier.nl/locate/jnucmat

Influence of low-temperature air oxidation on the dissolution behaviour of high burn-up LWR spent fuel

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Received 18 August 2000; accepted 4 December 2000

Abstract

High burn-up (53.1 GWd/t(U)) light water reactor (LWR) spent fuel (UO_2), previously oxidised in flowing air to O/M ratios varying from 2.0 to 2.44 (U_4O_{9+x}), was sequentially leached in deionised water at room temperature. A clear increase in the leaching rate of the matrix and fission products with a high redox sensitivity, like technetium and molybdenum, was observed as a function of the degree of oxidation. This effect is limited to the initial step of leaching and was not observed for plutonium and for subsequent leaching periods, no relevant influence of the O/M ratio on the leaching rate could be detected. For the uranium matrix, a very low leaching rate ($<3 \times 10^{-7}$ g cm^{-2} d^{-1}) was measured independent of the O/M ratio. In comparison to the matrix, all the fission products have higher release rates, suggesting a non-congruent leaching of elements segregated to the grain boundaries. © 2001 Elsevier Science B.V. All rights reserved.

PACS: 82.65.M; 81.65.M

1. Introduction

The direct disposal of spent fuel as a waste form is currently under consideration in many countries. As a possible accident scenario in a repository situated above the water table, failure of the fuel cladding during storage, with air coming into contact with the spent fuel, can be hypothesised. In this case, the spent fuel will be partially oxidised with the consequent chemical and/or physical degradation of the fuel [1–6].

In recent papers influence of the oxidation state on the leaching behaviour of spent fuel has been studied [2,3]. Dissolution tests on light water reactor (LWR) spent fuels, irradiated at different burn-ups and oxidised to U_4O_{9+x} or U_3O_8 were performed. Air oxidation up to U_4O_{9+x} was determined to have little effect on the uranium dissolution rate at moderate burn-up, while a more pronounced effect on the leaching rate of high burn-up fuels was established. The differences have been attributed to the nature and extension of fuel restructuring. On the other hand, a dramatic effect was found for the fuel oxidised to U_3O_8 where, e.g., the dissolution rate of caesium amounted to as much as 12% of the inventory during the first day [3]. In fact, oxidation to or beyond U_3O_8 may cause a severe physical degradation due to density decreases, leading to the production of fine powder due to the opening of grain boundaries, with a consequent increase in the surface available for leaching [6].

Taking into account the trend of the nuclear industry towards increased discharge burn-ups and the increasing use of mixed oxide fuels (MOX) in Europe, a research programme was started to investigate the influence of oxidation on the dissolution behaviour of these types of LWR spent fuels in deionised water. The present paper

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reports the leaching behaviour of irradiated UO_2 after low-temperature air oxidation.

2. Experimental

2.1. Oxidation test

The samples used in the present study were LWR UO_2 spent fuel (53.1 GWd/t(U)) pieces previously oxidised in flowing dry air at 270°C. The initial weight of the samples was approximately 300 mg. As seen by the weight gain as a function of time, an initial (very fast) oxidation occurs and is followed by a plateau [7]. If it is assumed that all the weight change is due to the oxygen reaction with the fuel, the evolution of the O/M ratio can be calculated. Fig. 1 shows the oxidation curve of the fuel tested [7]. The fuel samples selected for the leaching tests are marked on this curve: non-oxidised spent fuel (sample A) and oxidised samples with a O/M ratio of 2.35 (sample B), 2.39 (sample C) and 2.44 (sample D).

2.2. Leaching test

The leaching tests were performed in deionised water in air atmosphere at the ambient temperature of the hot cell (about 25°C). The surface/volume ratio (S/V) was approximately 2 m^{-1}, where the surface corresponds to the geometric surface assuming an ideal spherical form of the sample. Successive steps of the experimental procedure can be schematically described as follows:

(a) The specimens were immersed in 20 ml of water in 50 ml glass bottles. The bottles were kept closed during each run.

(b) After completion of each contact period (1, 7, 15, 50 and 150 days), the specimens were transferred to a new bottle with fresh leachant.

(c) The empty used bottles were rinsed with 1 M HNO_3, and the rinse solutions were analysed separately.

2.3. Chemical analysis of the leachates: sample preparation and procedure

Chemical analysis of the leachates and rinse solutions was performed by ICP-MS (ELAN 5000, Perkin ElmerSciex) installed in a glove-box and modified in order to handle radioactive samples. The measurements were performed in the mass ranges 80–160 and 230–245.

Dilution of the samples, when required, was done using 1 M HNO_3 (Merck, Suprapur) and Elgastat UHQPS ultrapure water (ELGA). Indium, terbium and thorium were used as internal standards at a concentration level of ca. 50 ppb.

3. Results and discussion

Figs. 2–7 show the amount of the main fission products and actinides found in solution, expressed as a fraction of the fuel inventory. The data points in these figures represent the total released fraction of each element, including leachate and rinse solution. The inventory was obtained from KORIGEN code calculations.

3.1. Actinides

In Fig. 2 the uranium fractional release is shown. The four samples with various O/M ratios presented the same behaviour: high dissolution rate at the beginning, decreasing to a very low value after 30 days. The ura-

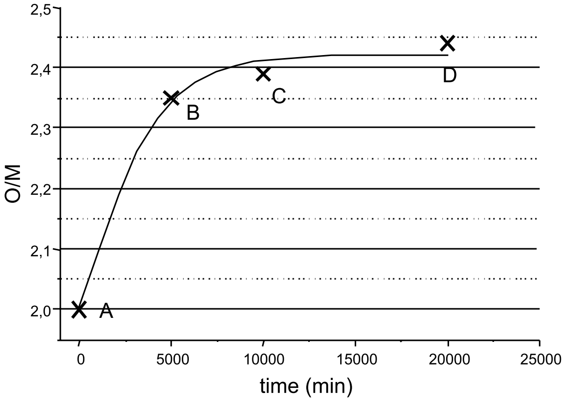

Fig. 1. Curve of oxidation of the fuel tested (7) and the O/M ratio of the fuel samples utilised for the leaching tests (samples A, B, C and D).

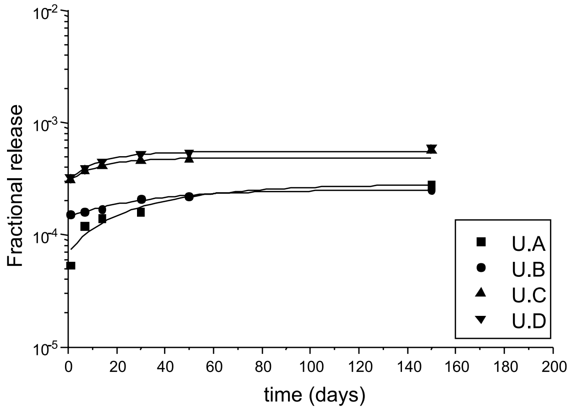

Fig. 2. Cumulative fractional release for uranium-238 as a function of contact time.

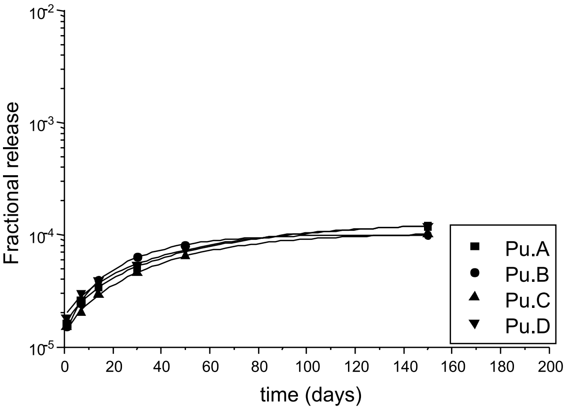

Fig. 3. Cumulative fractional release for plutonium-239 as a function of contact time.

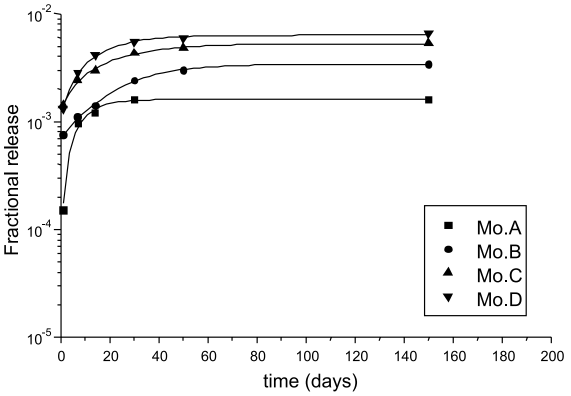

Fig. 4. Cumulative fractional release for molybdenum-98 as a function of contact time.

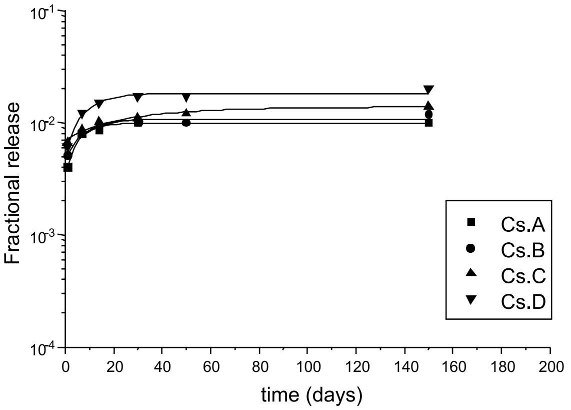

Fig. 5. Cumulative fractional release for caesium-137 as a function of contact time.

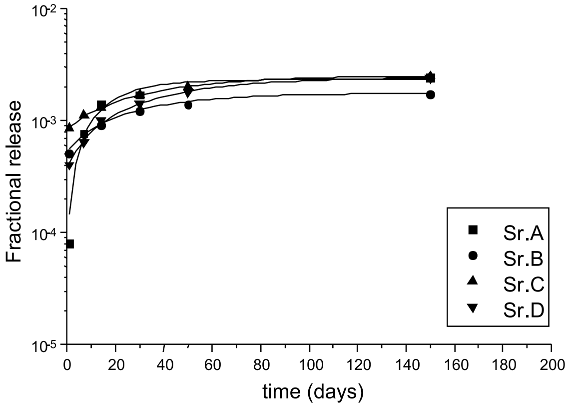

Fig. 6. Cumulative fractional release for strontium-90 as a function of contact time.

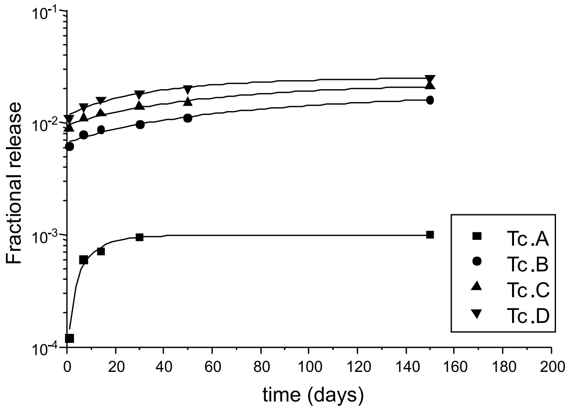

Fig. 7. Cumulative fractional release for technetium-99 as a function of contact time.

nium fractional released for the first contact period (1 day leaching) for the two higher O/M ratios (samples C and D) is about one order of magnitude higher than for the least oxidised fuel. This behaviour is clearly related to the oxidation level of the fuel (see Fig. 1). In fact, samples C and D belong to the plateau, a steady zone of U_4O_{9+x}, while sample B is situated in the zone with relatively low O/M ratio, where the oxidation process has not yet affected the leaching behaviour.

In Table 1 the uranium leaching rates at the first leaching interval and at the end of the experiment for the four O/M ratios tested are given. Again the clear effect of oxidation on the leaching rate at the beginning of the process is illustrated; the differences between the non-oxidised fuel and the oxidised fuel amount to one order of magnitude. On the other hand, for subsequent leaching periods, no relevant influence of the O/M ratio on the leaching rate could be measured, with the uranium matrix leaching rate decreasing to the very low

Table 1
Uranium leaching rates at the initial step of leaching, 1 day, and between 25 and 150 days, for samples A, B, C and D

Time (days)	Uranium leaching rate (g cm^{-2} d^{-1})[a]			
	A	B	C	D
0–1	1.5×10^{-5}	9.9×10^{-5}	1.7×10^{-4}	1.6×10^{-4}
25–150	2.6×10^{-7}	2.1×10^{-7}	1.4×10^{-7}	1.09×10^{-7}

[a] Rate obtained from geometrical surface assuming an ideal spherical form of the sample.

value of 3×10^{-7} g cm^{-2} d^{-1}. A slight decrease rate of the leaching rate with the oxidation level (up to U_4O_{9+x}) observed in the steady-state region cannot be attributed to a solubility limited dissolution, since fresh leachate was used for each leaching period.

It is important to note from the point of view of safety that low values of leaching rates showed in Table 1 would be even lower if they would have been calculated as a function of the real fuel surface, since the geometric area used for the calculations is generally much lower than the actual surface. The present study confirms the high chemical stability of irradiated UO_2 to the water attack, also after oxidation up to U_4O_{9+x}.

In contrast to uranium, the plutonium concentration release (Fig. 3) is not affected by the fuel oxidation state, not even at the beginning of the dissolution process. Plutonium concentrations were between 1×10^{-8} and 1×10^{-9} M, whose values are in good agreement with those found for non-oxidised fuels [6].

3.2. Fission products

Molybdenum is found in the fuel as metallic precipitate (ϵ-phase) or oxide precipitate at the grain boundary [8]. The fractional release of molybdenum is one order of magnitude higher than that of uranium, indicating an increased amount of this element at the surface in contact with the leachant, probably due to segregation to the grain boundaries upon irradiation. The differences of molybdenum releases observed for the different O/M ratios tested indicate sensitivity of this element to the oxidation level of the fuel similar to uranium (Fig. 4), with one order of magnitude difference in the leached amount between the fuel having the greatest O/M ratio and the non-oxidised one. The concentration of molybdenum in the mentioned ϵ-phase decreases continuously due to the buffer properties of this element, making it prone to react with the oxygen excess produced during the fission process [9]. In the fuel used in this work, due to its high burn-up and the subsequent oxidation treatment, it can be assumed that most of the molybdenum present at the grain boundary is already oxidised in the samples B, C and D.

Caesium is known to migrate towards matrix grain boundaries and crack surfaces during the reactor operation [8]. This element shows an instant fractional release about two orders of magnitude higher than that of uranium (Fig. 5), confirming a strong migration of this element during irradiation. The differences in the oxidation levels of the matrix studied are much less pronounced than for uranium and molybdenum probably because caesium cannot be further oxidised beyond the level attained during irradiation.

Strontium is a fission product that can be found partly dissolved as an oxide in the spent fuel matrix, with only a small fraction precipitated as a component of the perovskite oxide phase [8]. This element shows release values between those of uranium and caesium (Fig. 6). As in the case of caesium, no relevant differences between the different O/M ratios have been observed again due to the absence of redox reactions of strontium.

Technetium is a highly mobile element, especially under oxidising conditions, constituting a potential danger to the biosphere due to its migration in case of water flooding of a repository [10]. The technetium fractional release given in Fig. 7 was calculated from the total inventory of technetium present in the fuel but, parallel experiments of total dissolution of this fuel, have shown that about 40% of the technetium cannot be dissolved even in high acid concentration. This means that only a small part of technetium is available for leaching and, consequently, that the fractional release would be increased by 60%. The large increase of the release at high oxidation has been attributed to the high sensitivity of technetium to oxidation (TcO_4^-). In fact, a difference almost two orders of magnitude was measured between the oxidised and the untreated samples.

In order to compare the release rates of different fission products and actinides, the fractional release was normalised to uranium for each element. The normalised fractional release (FRN) is shown in Fig. 8 (non-oxidised fuel) and 9 (fuel with highest oxidation degree). In both cases no congruent leaching of the fission products was observed ($\text{FRN} \geqslant 1$). The increased fractional release of all fission products measured in comparison to the matrix can be attributed mainly to two effects: (1) a higher fission product inventory of the fuel at the grain boundaries and thereby easier to be leached; (2) a higher solubility of some fission products like technetium (as TcO_4^-) or caesium.

The FRN of plutonium is lower than 1, indicating that no migration during irradiation occurred and re-

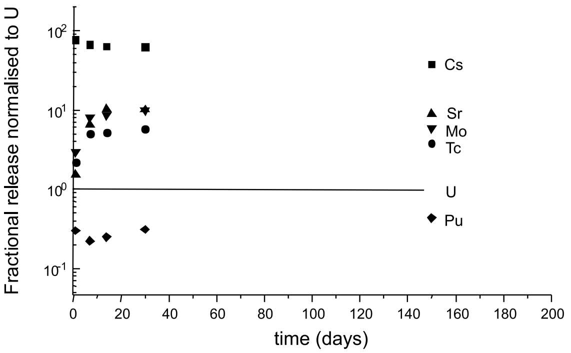

Fig. 8. Fraction release normalised to uranium for untreated fuel (sample A).

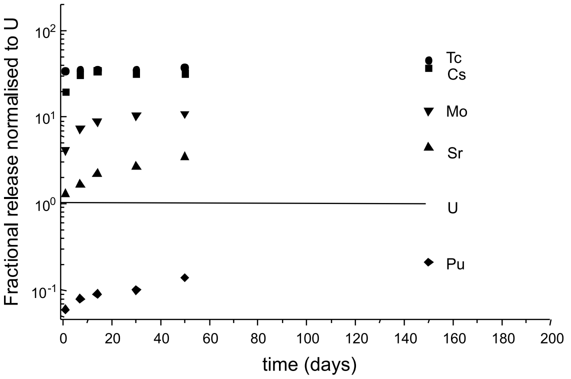

Fig. 9. Fraction release normalised to uranium for the most oxidised fuel used in this work (sample D).

flecting the fact of its very low solubility. As expected, comparing the samples A (non-oxidised) and D (highest oxidation), big differences were observed for fission products with high redox sensitivity such as molybdenum and, specially for technetium. Caesium and strontium show slightly lower FRN values, that of molybdenum is slightly higher, and the technetium value is even increased by a factor 10 for the oxidised fuel.

4. Conclusions

Experimental results of the present study indicate that pre-oxidation of high burn-up UO_2 spent fuel in air has a significant effect on the instantaneous release of uranium and fission products. After 1 day contact time, differences of about one order of magnitude between the fuel having the greatest O/M ratio and the non-oxidised fuel were found for uranium. After this initial stage, a very low leaching rate ($<3 \times 10^{-7}$ g cm^{-2} d^{-1}) was measured independent of the oxidation level. The plutonium release was not affected by the fuel oxidation state and shows a fractional release which is about 10 times lower as compared to uranium. All the fission products show a higher fractional release as compared to the matrix. This effect has been attributed to segregation upon irradiation of these elements to the grain boundaries.

Acknowledgements

This work has been carried out at the Institute for Transuranium Elements of Karlsruhe (Germany) in the frame of an agreement for scientific-technological collaboration between the European Commission (ITU-JRC), CIEMAT and ENRESA. The authors would like to thank Mr Teixeira and Mr Nicholl for their sample preparation and Mr Pagliosa and Mr Römer for their invaluable help in performing the leaching experiments in a hot cell.

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