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Gap and grain boundaries inventories from pressurized water reactor spent fuels

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Abstract

To assess the long term behaviour of spent fuel in a French nuclear waste repository, the chemical reactions between the fuel and possible intruding water must be understood and the resulting radionuclide release must be quantified. The instant release fraction source term, assumed to be instantaneously accessible to water after the failure of the waste container and the saturation of the engineered barrier, includes the soluble radionuclides (RN) located within the gap, the fractures and grain-boundary areas. At first, to provide an estimate of the potential RN releases from French PWR spent fuels, Cs and Sr inventories from the gap region have been measured on different UOX and MOX fuel samples (20 mm segments of clad fuel rods) as a function of the Burnup (from 22 to 60 GW d t^{-1}) and the fission gas releases (FGR). Moreover and because of a lack of knowledge on high Burnup fuels, a specific measurement of grain boundary inventories has been carried out on a spent fuel with a Burnup of 60 GW d t^{-1} and 2.8% of FGR. Leaching experiments have been made under pseudo dynamic conditions in a presence of carbonates on a powder 20–50 μm in size. The chemical and radiochemical analysis of the different samplings show that the Cs grain boundary inventory is less than 0.4% of the total Cs inventory whereas the Cs gap release is about 1%. The estimated Sr grain boundary inventory is less than 0.2% of the total Sr inventory. Theses results are also compared with the literature data.

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1. Introduction

For a potential performance assessment of direct disposal of spent fuel in a nuclear waste repository, the chemical reactions between the fuel and possible intruding water must be understood and the resulting radionuclide release must be quantified. Two source terms are distinguished today: the instant release fraction (IRF), assumed to be instantaneously accessible to water, and the radionuclides released by alteration of the UO_2 grains.

This article discusses experimental work on the quantification of the instant release fraction source term for French UOX and MOX fuel. It is generally acknowledged that this source term comprises at least the radionuclide fraction in the gap, in the cracks and at the grain boundaries of a spent fuel rod. For performance assessment purposes, various approaches with varying degrees of conservatism have been developed – even to the point of including in the labile fraction the contribution of radionuclides in the rim for high burnup (>40 GW d t^{-1}) UOX fuel and in the aggregates for MOX fuel.

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Available experimental data are very limited and some values have are missing, notably for quantifying the labile inventories at the grain boundaries or in the rim of high burnup fuel.

This article provides data on the cesium and strontium inventories in the gap and cracks for UOX fuel with burnup values ranging from 22 to 60 GW d t^{-1} and for MOX fuel with a burnup of 47 GW d t^{-1}. Data are also presented on the inventory at the grain boundaries for high burnup (60 GW d t^{-1}) UOX fuel.

2. Experimental

2.1. Gap inventory for UOX 22 to 60 GW d t^{-1} and MOX 47 GW d t^{-1}

The characteristics of the spent fuel samples are summarized in Table 1. From a heat transfer standpoint, the linear power values for the fuel samples were low, about 20 kW m^{-1}.

The fuel radionuclide inventories as of the date of the leaching experiments were calculated using CESAR code [1].

The gap inventories were determined by static mode leaching experiments in carbonated water ($[HCO_3^-] = 10^{-3}$ M) with 20 mm clad segments. The tests, under air atmosphere, lasted 62 with solution samples taken at the following intervals: 3, 10, 24 and 62.

2.2. Grain boundary inventory for UOX 60 GW d t^{-1}

Experiments to determine the inventory at the grain boundaries were carried out only on UOX PWR fuel with a burnup of 60 GW d t^{-1} with the characteristics indicated in Table 1. Leaching experiments were carried out on fuel powder according to a protocol similar to the one developed and validated by Gray [2,3].

2.2.1. Powder samples

Spent fuel fragments were sampled from the center of a clad 35 mm segment previously leached for one week in carbonated water ($[HCO_3^-] = 10^{-3}$ M) to eliminate the gap inventory. Sampling the fragments at the center of the segment also eliminated the contribution of the rim.

We decided not to prepare the powder samples after prior oxidation of the spent fuel fragments in air at low temperature (about 463 K); this method leads to the formation of U_4O_9 around the periphery of the grains, which embrittles the grain boundaries and facilitates the powder preparation but can also affect the radionuclide distribution and release [2]. Powder samples with a particle size fraction of 20–50 μm were therefore prepared by grinding and sieving in a hot cell. The number of grains in each particle was estimated at about forty.

2.2.2. Leaching experiments

Pseudo-dynamic leach tests, under air atmosphere in hot cell, were carried out on 567 mg of powder in 25 mL of carbonated water ($NaHCO_3 \times 10^{-2}$ M) to prevent any precipitation of uranium used as a matrix alteration tracer. After each cycle the solutions were filtered and analyzed. Fresh water was added to the leaching reactors.

Thirty cycles were carried out, initially of short duration (1–2 h) to avoid any precipitation resulting from leaching of the oxidized UO_{2+x} layer, then longer (24–48 h). The variation of the ratios

Table 1
Spent fuel irradiation characteristics

PWR fuel type Burn up (GW d t^{-1})	UOX22 22	UOX37 37	UOX47 47	UOX60 60	MOX47 47
Reactor	Bugey 3	Bugey 3	Fessenheim 2	Gravelines 2	St Laurent B1
Fuel assembly	FGA 54	FGC 53	FEC 57	FF06E3BV	FFPOOHJX
Position in assembly	H 09	J 09	H 11	J 07	L 14
Initial ^{235}U ratio (%)	2.1	3.1	3.1	4.5	0.244
Initial Pu fraction (%)	–	–	–	–	5.6
Reactor cycles	1	3	4	5	3
Irradiation history					
Begin	31 August 78	31 August 78	27 June 77	20 November 83	December 87
End	14 September 80	4 February 82	4 January 83	6 May 89	January 91
Mean burnup (GW d t^{-1})	20.4	35.2	45.79	57.6	41.3
Fission gas release (%)	0.1	0.2	0.5	2.8	6.8

of the fraction of inventory in aqueous phase $FIAP_{\mathrm{Cs}}/FIAP_{\mathrm{U}}$ and $FIAP_{\mathrm{Sr}}/FIAP_{\mathrm{U}}$ are used to estimate the inventories at the grain boundaries, hence the importance of preventing uranium precipitation. When the ratio of the released fractions is equal to 1 it may be assumed that the complete inventory at the grain boundaries was leached during the preceding cycles.

2.3. Solution analysis and calculation of release fractions

Classical radiometric techniques such as β counting and gamma spectrometry were used to determine strontium (^{90}Sr) and cesium (^{134}Cs and ^{137}Cs). Uranium was assayed using a laser-induced kinetic phosphorescence analyzer (KPA). This technique is capable of determining concentrations between 0.5 and 100 μg L^{-1}, i.e. 2.1×10^{-9}–4.21×10^{-7} mol L^{-1} of uranium.

For a radionuclide X, the inventory fraction released in the aqueous phase (*FIAP*) is expressed as follows:

$$FIAP_{\mathrm{X}} = \frac{A_{\mathrm{sol}}^{\mathrm{X}} V_{\mathrm{sol}}}{A^{\mathrm{X}} f_{\mathrm{U}} m_{\mathrm{UO_2}}}, \tag{1}$$

where

$A_{\mathrm{sol}}^{\mathrm{X}}$: specific activity of radionuclide X in aqueous phase in the leachate (Bq mL^{-1}).
A^{X}: specific activity of radionuclide X in initial spent fuel inventory (Bq g(U)$^{-1}$).
V_{sol}: volume of solution (mL).
$m_{\mathrm{UO_2}}$: initial uranium oxide mass in spent fuel sample (g).
f_{U}: mass conversion factor of uranium metal per gram of fuel (for UOX and MOX).[1]

In the case of a test under static conditions (gap inventories), p samples are taken from the leaching vessel; it is more relevant to follow the variation of the cumulative fraction of inventory in the aqueous phase for a radionuclide (or element) X at interval n ($1 \leqslant n \leqslant p$), i.e. $\sum FIAP_{\mathrm{X}}(n)$, which is directly related to the total release from the sample since the beginning of the experiment. This quantity is calculated as follows for any radionuclide X:

$$FIAPc(n) = \sum FIAP_{\mathrm{X}}(n) = \frac{A_{\mathrm{sol}}^{\mathrm{X}}(n,n) V_{\mathrm{leachate}}(n) + \sum_{i=1}^{n-1} A_{\mathrm{sol}}^{\mathrm{X}}(i,n) V_{\mathrm{sample}}(i)}{A_{\mathrm{X}}(n) f_{\mathrm{U}} m_{\mathrm{UO_2}}}. \tag{2}$$

For experiments conducted under pseudo-dynamic conditions (grain boundary inventories) comprising p cycles, the cumulative fraction of inventory in aqueous phase of a radionuclide X after cycle n is expressed thus:

$$FIAPc(n) = \sum_{i=1}^{n} FIAP_{\mathrm{X}}(i). \tag{3}$$

3. Results and discussion

3.1. Gap inventory: UOX 22 to 60 GW d t^{-1} and MOX 47 GW d t^{-1}

Fig. 1 shows the variation of the cumulative release fractions of ^{134}Cs and ^{90}Sr over time for different UOX and MOX fuel samples.

From day ten and for UOX fuels these fractions stabilized and the labile release attributable to the gap could be quantified. A breakdown in the slope of the curves was observed and attribute to the end of gap and cracks release. After 20 days, a little decrease of integral release fraction was observed, showing grain boundaries release phenomenon.

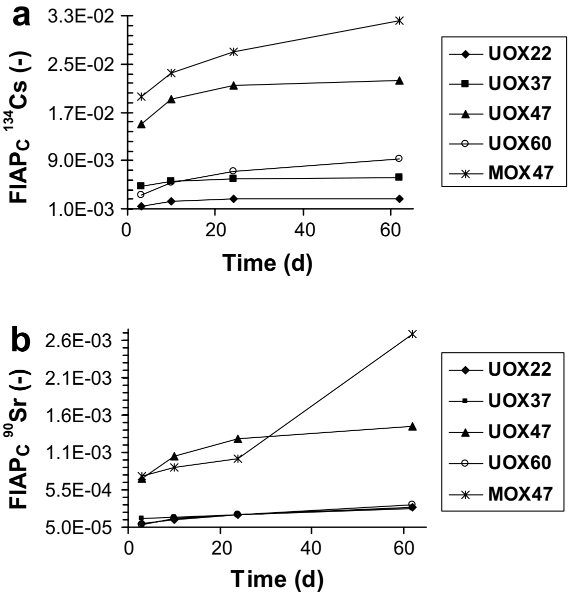

Fig. 1. Cumulative ^{134}Cs (a) and ^{90}Sr (b) release fractions (*FIAPc*) versus time (62 d) for spent UOX and MOX fuel segments.

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[1] For MOX, the heavy metal quantity taken into account includes the plutonium; the same conversion factor is used.

These two releases (gap and grain boundaries release) occur in a continuous way and cannot be strictly separated by this experiment. But as a consequence, the values obtained at day 62 are conservative ones.

The $^{134/137}$Cs gap inventory increased from 0.3% to 2.2% with the UOX fuel burnup up to 47 GW d t^{-1}. Conversely, and unlike the FGR (Table 2), the labile release from UOX60 fuel diminished to about 1%. The fact that the gap remained closed at room temperature for high-burnup fuel could account for the lower release [4]. Moreover, the labile release was generally less than observed with American (ATM-106) fuel, which is not surprising considering the significant differences in the FGR, particularly at high burnup. A higher labile release (about 3%) was observed for MOX47, and had not fully stabilized after 62 days.

The ^{90}Sr releases followed a similar trend, i.e. increasing from 0.03% to 0.15% with the burnup for UOX22, 33 and 47, with a decrease observed for UOX60 fuel (0.03%). The release obtained for MOX fuel was about 0.25% after 62 days.

The mean labile release was higher in the MOX fuel sample than in the UOX samples. Several factors could account for this difference:

- the greater reactive surface area of MOX fuel arising from its highly porous 'cauliflower' structure in the plutonium-rich agglomerates with locally high burnup;
- concentration of the strontium and cesium inventory in the plutonium-rich agglomerates, in conjunction with preferential leaching of these agglomerates;
- greater alteration of the $(U,Pu)O_2$ matrix.

It is difficult to identify the most likely hypothesis at this time.

3.2. Grain boundary inventory: UOX60

Fig. 2 shows the analysis results expressed as cumulative release fractions over all the cycles for the following elements or radionuclides: ^{134}Cs, ^{90}Sr and U. The first six one-hour cycles show that the cumulative cesium and strontium release fractions in solution were clearly higher than for uranium, the fuel matrix dissolution tracer. The variations were substantially lower during the subsequent cycles and all had the same slope indicating that the fission product release was controlled by uranium.

The variation of the $FIAP_{Cs}/FIAP_{U}$ and $FIAP_{Sr}/FIAP_{U}$ congruence ratios (Fig. 3) also shows that these ratios tend toward 1 after the sixth leaching cycle; this confirms the major contribution of the UO_2 matrix in Cs and Sr release after the sixth cycle.

After subtracting the uranium release fraction, the Cs and Sr inventories at the grain boundaries were determined to be 0.38% and 0.18 wt%, respectively, for UOX fuel with a burnup of 60 GW d t^{-1}. As the total relative error on the analysis values did not exceed 10%, the absolute error on the inventory determinations can be considered within ±0.07% for cesium and ±0.05% for strontium.

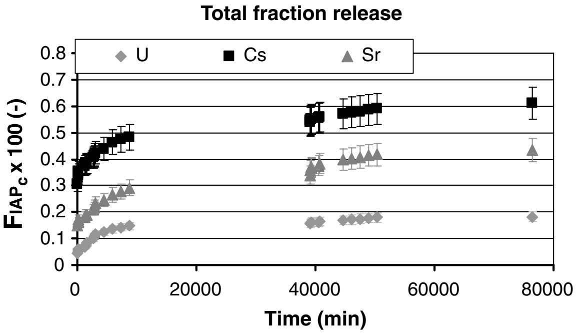

Fig. 2. Cumulative ^{134}Cs, ^{90}Sr and U release fractions versus time at the grain boundaries of UOX60 fuel.

Table 2
Data concerning the instant release fraction in various nuclear fuel samples

Fuel type	Burnup (GW d t^{-1})	FGR (%)	Cs gap (%)	Cs GB (%)	Sr gap (%)	Sr GB (%)
UOX22[a]	22	0.14	0.27	nd	0.025	nd
UOX37[a]	37	0.23	0.66	nd	0.04	nd
UOX47[a]	47	0.41	2.2	nd	0.15	nd
UOX 60[a]	60	2.8	1	0.38	0.03	0.18
MOX47[a]	47.5	7	3.2	nd	0.25	nd
ATM104[b]	44	1.1	1.2	0.1	nd	nd
ATM106[b]	43	7.4	2	0.5	0.11	0.03
ATM106[b]	50	18	6.5	1	0.1	0.07

[a] This work.
[b] From Ref. [5].

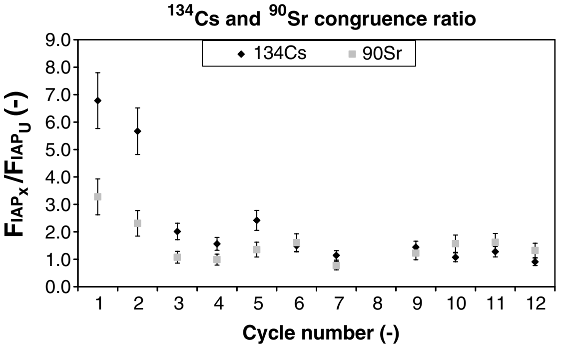

Fig. 3. Grain boundary release fraction ratios for $FIAP_{Cs}/FIAP_U$, $FIAP_{Sr}/FIAP_U$ after each leaching cycle for UOX60 fuel.

It may also be noted that the $FIAP_{Cs}/FIAP_U$ congruence ratios after each cycle were always greater than 1, even after many leaching cycles. As each particle consisted of about 40 grains, a residual inventory cannot be ruled out, nor can the possible existence of a concentration gradient around the periphery of the UO_2 grains [2].

The dissolution rate of the fuel grains can be estimated for the final cycles, i.e. after complete elimination of the oxidized layer. The calculated dissolution rate under these conditions was estimated at 0.5 mg m^{-2} d^{-1}, which is consistent with the findings reported by Gray under dynamic conditions [2].

3.3. Labile inventory (gap + grain boundaries): UOX60 fuel

The new data concerning the $^{134/137}$Cs and ^{90}Sr inventories at the grain boundaries thus allow us estimate the labile inventory of UOX60 fuel a few years after removal from the reactor. The labile cesium inventory (gap + grain boundaries) is about 1.4% (1% in the gap and 0.4% in the grain boundaries); the corresponding figures for ^{90}Sr are about 0.21% (0.03% in the gap and 0.18% in the grain boundaries). These values are lower than the most optimistic predictions by Johnson et al. [5] (10% and 3%, respectively, for UOX60). The difference is attributable mainly to the hypotheses assumed by Johnson for estimating the labile inventory, together with uncertainties on the long-term behavior of the rim in particular (a thermal diffusion, opening of grain boundaries). In our investigation of fuel recently removed from the reactor (with a burn up of 60 GW d t^{-1}), the fission products in the rim remained inaccessible to water (closed gap, closed porosity).

4. Conclusion

This article provides data on the cesium and strontium inventories in the gap and cracks for French UOX fuel with burnup values ranging from 22 to 60 GW d t^{-1} and for MOX fuel with a burnup of 47 GW d t^{-1} (Table 2). These findings are consistent with published data, but reveal no clear dependence with the burnup and FGR, as determined on CANDU type fuels in [6].

Data concerning the grain boundary inventory for high burnup UOX fuel (60 GW d t^{-1}) were also used for first time to estimate the labile inventory (gap + cracks + grain boundaries) in this type of fuel. The labile cesium inventory is about 1.4% and the labile ^{90}Sr inventory about 0.21%.

These experimental results confirm the advantage of pursuing this study both in the rim zones for which data are currently lacking, and in MOX fuel while discriminating the Pu aggregates. Ultimately the accessibility of this labile inventory to water over time can be estimated from studies of helium accumulation at the grain boundaries (stable or not) and athermal diffusion during spent fuel evolution in a closed system.

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