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Spent fuel radionuclide source term model for assessing spent fuel performance in geological disposal. Part II: Matrix alteration model and global performance

Christophe Poinssot [a,*], Cécile Ferry [a], Patrick Lovera [a],
Christophe Jegou [b], Jean-Marie Gras [c]

[a] *Commissariat à l'Energie Atomique (CEA), Nuclear Energy Division, CEA Saclay, Department of Physics and Chemistry, Service for the Studies of the Radionuclides Behavior, DPC/SECR, BP.11, F-91191 Gif-sur-Yvette cedex, France*
[b] *Commissariat à l'Energie Atomique (CEA), Nuclear Energy Division, Department of Waste Treatment and Conditioning, Service for the Studies of the Conditioning Material Behavior, DTCD/SECM/LMPA, CEA Marcoule, France*
[c] *Electricité de France (EDF), R&D Division, Les Renardières, France*

Abstract

In the framework of the research conducted on the long term evolution of spent nuclear fuel under geological disposal conditions, a source term model has been developed to evaluate the instantaneous release of radionuclides (RN) (instant release fraction, IRF) and the delayed release of the RN which are embedded within the matrix. This model takes into account most of the scientific results currently available except the effect of hydrogen and the current knowledge of the uncertainties. IRF was assessed by considering the evolution with time of the RN inventories located within the fuel microstructure to which no confinement properties can be allocated over the long term (gap, rim, grain boundaries). This allows for bounding values for the IRF as a function of time of canister breach and burnup. The matrix radiolytic dissolution was modeled by a simple kinetic model neglecting the recombination of radiolytic species and the influence of aqueous ligands. The oxidation of the UO_2 matrix was assumed not to be kinetically controlled. Spent fuel performance was therefore demonstrated to mainly depend on the reactive surface area.

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1. Introduction

Direct disposal is being studied in many countries as a possible way to manage commercial spent nuclear fuel (CSNF). Although the reprocessing of spent fuel is clearly the reference scenario for the management of spent fuel in France, only two thirds of the total annual budget of spent nuclear fuel are currently reprocessed in order to meet the need for the Pu recovered by reprocessing and recycled as MOX fuel: ~350 tHM y^{-1} are currently stored waiting for further decision, delayed reprocessing, long-term storage or ultimate disposal. These stored fuels are either MOX or relatively high

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[*] Corresponding author. Tel.: +33 1 6908 3260; fax: +33 1 6908 5254.
E-mail address: christophe.poinssot@cea.fr (C. Poinssot).

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burnup UOX fuels ($\geqslant 47.5\,\mathrm{GWd\,t^{-1}}$) since lower burnup CSNF has already been reprocessed in the past years. The 1991 French law on nuclear waste management has required the direct disposal of CSNF to be studied as a potential option for the back-end of the fuel-cycle [1]. The aim is to bring to the political and industrial stakeholders all the available scientific and technical information on spent nuclear fuel long-term evolution and related performances, in order to help them to potentially make decisions about the final fate of commercial spent nuclear fuel in 2006.

In this context, one of the major expected input from the research on CNSF is to have a robust and reliable model to describe the progressive and slow release of radionuclides (RN) from the fuel packages under deep repository conditions [2–4]. These models are therefore to be used in subsequent performance assessments and safety analyses in order to evaluate the long term impact of potential geological disposal. The models have to account for all the available knowledge on CSNF long term evolution and simultaneously to consider, as necessary, some conservative assumptions to avoid an underestimation of RN release. Indeed, safety analyses have specific requirement in the sense that they need to be robust towards the current uncertainty or lack of knowledge on all the relevant mechanisms and parameters.

Experiments performed on CSNF since the late 1970s demonstrated that the release of RN from spent nuclear fuel proceeds by two consecutive processes [5]:

(i) A relative instantaneous release of radionuclides, often referred to as the instant release fraction (IRF), which dominates the short term release. This fraction is usually released in laboratory experiments in some months and progressively decreases. This release is assumed to be related to the radionuclides (RN) which are located within the zones of the rod which have no retention capacity when water arrives at the contact of the fuel in the canister. These zones are described in the literature as being the gap interface between the cladding and the pellet, the fractures and part of the grain boundaries. Experimental results indicate that these radionuclides correspond roughly for fresh fuel to 3–5% of the total inventory [for example 6].

(ii) A slow long-term RN release which is often referred to as the matrix contribution. This is assumed to correspond to the release of the RN which are embedded within the uranium dioxide matrix. They are therefore released through the dissolution of the matrix. Reference conditions in geological repository in France are strongly reducing (~ -200 mV) and groundwaters are dominated by carbonates and silicates [7]. Under these conditions, spent fuel matrix has been assumed to be corroded through the radiolytic dissolution linked to the existence of a significant α radiolysis at the fuel/water interface [8,9]. Much effort has been put in the last years to build a reliable matrix alteration model including the radiolytic dissolutions [for example 10].

Published performance assessment (PA) calculations demonstrate the strong impact of the IRF on the doses arising from direct disposal [11,12]. The IRF is indeed mainly composed of weakly sorbing and highly mobile long-lived radionuclides such as ^{129}I, ^{36}Cl and ^{135}Cs.

The first part of this paper [13] presents the current generic IRF model developed by CEA and NAGRA in the framework of the SFS European project (FIKW-CT-2001-00192 SFS; [14]). The second part more specifically focuses: (i) on the matrix alteration model developed in France to describe the RN release from the CSNF under geological disposal conditions and (ii) the subsequent anticipated spent fuel performance in geological disposal.

2. Phenomenology of spent fuel alteration under disposal conditions

2.1. Identification of the processes involved in the CSNF alteration

The release of radionuclides from the CSNF matrix will be controlled by the rate at which the uranium matrix is corroded. Although uranium is sparingly soluble under reducing conditions similar to those encountered in a repository site [15], its solubility can increase significantly at the UO_2/water interface because of the $\alpha\beta\gamma$ irradiation field. Indeed, water radiolysis produces both oxidizing and reducing primary species as radicals ($OH^\bullet$, $HO_2^\bullet$, e^-_{aq}, $H^\bullet$) or in molecular form (H_3O^+, H_2, H_2O_2) at concentrations that depend on the nature of the radiation (α or $\beta\gamma$) and on the dose deposited in the water [16]. O_2 is not a primary radiolytic specie but comes from the recombination of primary species or dismutation of H_2O_2. Radiolysis can therefore lead to the onset of oxidizing conditions at the UO_2/water interface (redox disequilibrium with the environment) and accelerate the dissolution of the spent fuel matrix under disposal conditions. The French reference scenario of deep repository does not anticipate any water intrusion within the canister before at least 10 000 y except in a few defective canisters. This time is related to the time needed for water to resaturate the engineered barrier system and corrode the canister before reaching the spent fuel assembly. Therefore, except for the off-normal scenario of early breaching, water will then contact the spent fuel after βγ radiations significantly decreased by more than three orders of magnitude lower than the α radiation, which will dominate the radiation field for several 100 000 years (Fig. 1).

Alpha particles, the mean energy of which is ~5.25 MeV for CSNF, have a high linear energy transfer (LET) and will therefore transfer their energy to water over a limited distance which is estimated to be <45 μm from the fuel surface [17]. In addition, α radiolysis favors the formation of molecular species such as H_2O_2, H_2 or O_2 instead of radicals. These molecules will be directly produced close to the CSNF surface and part of them will subsequently react with the fuel surface, oxidizing U(IV) to U(VI). The global balance of this process is the formation of an oxidative layer at the fuel/water interface (UO_{2+x} with $0 < x < 0.33$) [8,9,11]. Subsequently, water ligands (OH^-, HCO_3^-, ...) will lead to the release of U(VI) into the solution and the formation of inorganic complexes. Carbonates have been in particular demonstrated to significantly favor the release of U(VI) in solution [12]. Aqueous uranium may then precipitate either locally on the fuel surface or further in the near-field, depending on the global redox balance (significance of the water volume which is oxidizing) and the water chemistry. Fig. 2 schematizes the successive processes involved in the CSNF alteration in deep repository.

Under repository conditions, experimental results have evidenced that the water radiolysis and the matrix oxidation are in most cases the limiting steps for the following reasons: (i) carbonates are significantly present within the environment and enhance the U(VI) release towards the solution, (ii) XPS measurements on un-irradiated UO_2 have shown the absence of a U(VI) layer [19,20] during UO_2 alteration in presence of carbonates. In addition, focusing on the first two steps is conservative in the sense that they will not lead to underestimation of the RN release rate. Most of the current research is therefore focused on the radiolysis and oxidation steps that are supposed to be the limiting ones.

2.2. Current status of CSNF alteration model development

Several works have been undertaken in the last years to quantify the specific influence of α activity on CSNF alteration and to develop scientific model to predict the long term alteration of CSNF [10,12,17,18,21–25]. These models aim to relate the alteration rate (*R*) to the α residual activity of the fuel (α dose rate and/or α dose and/or α specific activity), the fuel surface (reactive surface area *S*) and the physico-chemical conditions (T, P and water composition). The development of these models is based on two types of methodologies:

- *Electrochemical studies*: They use the electrochemical properties of UO_2 which allows to relate the corrosion potential to the corrosion rate [9,26]. This approach was in particular developed by the Canadian team [18,21,26]. They allow having specifically relevant information on the oxidation step.
- *Chemical studies*: They aim to measure along the experiments the evolution of the solution concentrations, in particular the uranium concentration, the

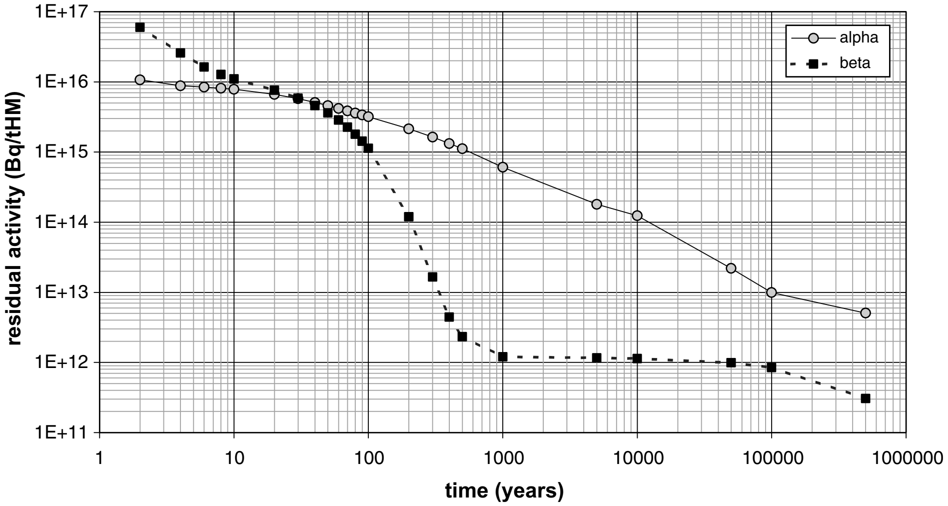

Fig. 1. Evolution of α, β and γ radiations as a function of time for a 55 GWd t^{-1} UOX fuel. Data are calculated from the CESAR isotopic evolution code [35].

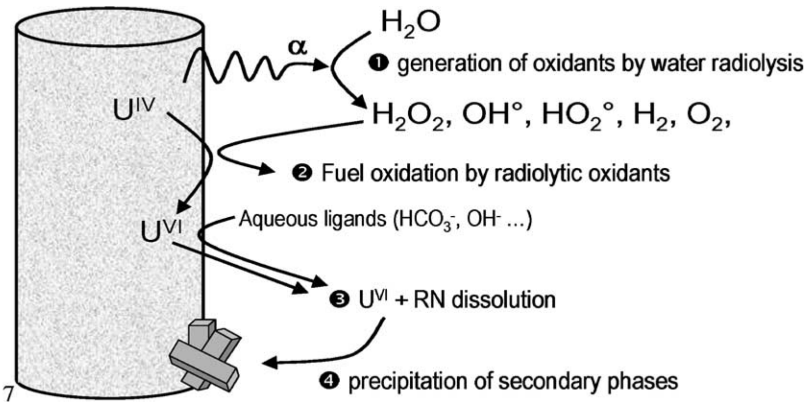

Fig. 2. Identification of the major processes involved in the spent fuel radiolytic dissolution at the fuel/water interface. Alpha particles entering in water produces radiolytic oxidants which subsequently oxidizes uranium in the spent nuclear fuel matrix. Uranium is therefore released through the aqueous ligands attachment. Finally, aqueous uranium can re-precipitate as secondary phases.

interpretation of which is not always straightforward since it supposes to deconvolute the respective influence of dissolution, U sorption, secondary phases precipitation, occurrence of colloids. Therefore, other elements are also commonly followed like Sr as they are supposed to be indicator of the matrix dissolution.

These methodologies are in particular applied on dedicated radiolytic experiments for which two main types can also be distinguished:

- *External irradiation experiments:* They are using external α source to produce the radiolytic species at the fuel/water interface. In particular, Sattonnay et al. [27] and Corbel et al. [28] use a $^4He^{2+}$ flux produced by a cyclotron to irradiate through thin UO_2 samples and reproduce hence the geometry of the fuel/water interface. These works demonstrate that (i) the dissolution rate can be related to the dose rate, (ii) the significant role played by H_2O_2 even though radicals have also to be accounted for.
- *Experiments with α-doped UO_2:* Initiated by Gray [29] and widely used since then, doping UO_2 with α emitters allows to strictly reproduce the processes involved in the fuel alteration, except for the cumulated dose and damages produced within the matrix. First results [29,30] clearly demonstrates the significant influence of the α flux on the pellet dissolution rates which increases by one or two orders of magnitude; However, no clear relation between the α activity and the dissolution rate was demonstrated. Conversely, the most recent results [30,31] demonstrate in deaerated conditions a good correlation between α flux and uranium release rate with rates ranging between 3 and 10^{-2} mg m^{-2} j^{-1}.

From these results, several types of models have been developed:

(i) An electrochemical model based on description of the UO_2 oxidation at the anode and oxidants reduction reactions at the cathode [18,21,26,32].
(ii) A chemical model based on the formalism of the mineral/water interface description developed by Stumm and focusing on the kinetics of surface complexes [20]; this model succeeds in reproducing the results of UO_2 dissolution in carbonate medium, but fails to reproduce data at low carbonate and oxygen content. This is interpreted as due to the absence of radiolytic models, which are more influencing under these conditions. However, this approach succeeds to rationalize most of the results available on unirradiated UO_2.
(iii) A more general model of radiolysis detailing the reactions occurring in the various zone of the fuel/water interface (zones irradiated respectively by γ, by βγ and by αβγ when approaching the fuel/water interface) [33]. This latter model considers the diffusion of the various species and the primary radiolytic yields to estimate the production of radiolytic species. It reproduces reasonably well the experimental dissolution rate and volumes of gases produced by radiolysis in deionised water on both α-doped and spent fuel [17,2]. However, some parameters have to be adjusted such as the H_2O_2 decomposition and the diffusion length of radicals. In addition, it is with difficulty applicable to more realistic models since it should include all the reactions between the various radiolytic species and the groundwater species, for most of which the kinetic constants are not

available. Finally, it contains more than 150 kinetic reactions coupled together and although it is a good research model, it has not been considered in the French approach as easily usable for long term prediction and PA calculations.

3. Assessment of the radionuclides release matrix alteration model

3.1. Modeling the radiolysis production of oxidants

CEA has developed a new spent fuel matrix alteration model for the performance assessment (PA). This model aims to quantify the RN release rates with robustness, avoiding any uncontrolled complexity, focusing on the most significant processes. It also aims to avoid any underestimation of the RN release and voluntarily stands therefore rather on the conservative side. It is based on all the available well-established results from the literature and the CEA research program [2–4,34,35]. Lastly, it aims to only use operational parameters, like burnups, which are accessible to the end-users and the implementers. In this context, water radiolysis at the fuel/water interface has been modeled by considering only the primary species in water (and therefore not oxygen) and the primary species as tabulated in radiolysis kinetic models [23]. Molecular and radicals oxidants are therefore assumed to be produced by alpha radiolysis and not consumed by any scavengers. In particular, reducing species have been neglected as well as any other aqueous species, and this is obviously conservative. Oxidative species considered are therefore H_2O_2 and radicals $OH^{\cdot}$ and $HO_2^{\bullet}$. The amount of radiolytic species produced by the fuel α activity has been conservatively estimated based on geometric consideration. The energy released into water E at the fuel interface is calculated by

$$\frac{dE}{dt} = \frac{1}{\eta} \cdot \overline{E}_\alpha \cdot A_v \cdot S \cdot L, \tag{1}$$

where S stands for the reactive surface area ($m^2\,g^{-1}$), E_α the average energy released by spent fuel α decays (5.25×10^6 eV particle^{-1}), A_v for the volume α activity of spent fuel (Bq g^{-1}), L for the mean path of α particles in the fuel matrix (12×10^{-6} m) and η a geometric factor accounting for the relative number of α particles produced within the volume ($S \times L$) which can reach water and produce oxidants while assuming that all the energy is deposited at the end of the pathway at the Bragg peak. If we assume that the fuel/water interface can be modeled by a 2-D surface (extension of the fragments $\gg L = 12$ μm in order to neglect the curvature) and thickness of the water layer is higher than 40 μm, the geometric factor equals 4, meaning 1/4th of the α particles reach water.

This energy is almost integrally transferred to water and produce radiolytic species which can be estimated using the primary radiolytic yield G_i:

$$N_{\text{oxidants}} = \sum_i \frac{dE}{dt} G_i. \tag{2}$$

These species are produced at a certain distance from the fuel/water interface, but within the first 45 μm which is the maximum penetration depth of α particles from the fuel surface [17].

3.2. Modeling the fuel oxidation

Oxidants have therefore to diffuse from where they are produced to the fuel surface in order to react with U(IV). This process is assumed to be isotropic which means that statistically, only half of the oxidants can reach the surface and oxidize the fuel since their lifetimes are short. Due to the lack of reliable and extrapolable experimental data, we conservatively assume that all the oxidants which reach the surface react with U(IV) to produce U(VI). This hypothesis is obviously very conservative but can hardly be avoided due to the lack of data on the influence of natural aqueous species (major and trace elements) on primary radiolytic species fate.

French reference site of Bure where an underground research laboratory is under construction is located in the Callovo-Oxfordian argilites at −500 m depth in a strongly reducing ($E_h \sim -200$ mV) and slightly alkaline (pH ~ 7–9) environment [7]. Around the fuel interface, a locally oxidizing environment is supposed to occur under the influence of radiolysis with $E_h > 200$ mV. In such an environment, uranium aqueous speciation is dominated by $UO_2(OH)_2$. Fuel oxidation can therefore be modeled by the following equations [23,25]:

$$UO_2 + HO_2 \rightarrow UO_3H + H_2O_2 - H_2O \tag{3}$$

$$UO_2 + H_2O_2 \rightarrow UO_3H + OH \tag{4}$$

$$UO_2 + OH \rightarrow UO_3H \tag{5}$$

$$2UO_3H \rightarrow UO_2(OH)_2 + UO_2 \tag{6}$$

Considering the global balance of uranium and oxidants, it can be demonstrated that

$$\begin{aligned}(3G_{HO_2} + 2G_{H_2O_2} + G_{OH}) \cdot UO_2 + G_{HO_2} \cdot HO_2 \\ + G_{HO_2} \cdot H_2O + G_{H_2O_2} \cdot H_2O_2 + G_{OH} \cdot OH \\ \rightarrow (3G_{HO_2} + 2G_{H_2O_2} + G_{OH}) \cdot UO_3H\end{aligned} \tag{7}$$

where G_i stands for primary radiolytic yield of specie i. Considering Eq. (6) and Eq. (5), it comes out:

$$\begin{aligned}\left(\frac{3}{2}G_{HO_2} + G_{H_2O_2} + \frac{1}{2}G_{OH}\right) \cdot UO_2 + G_{HO_2} \cdot HO_2 \\ + G_{HO_2} \cdot H_2O + G_{H_2O_2} \cdot H_2O_2 + G_{OH} \cdot OH \\ \rightarrow \left(\frac{3}{2}G_{HO_2} + G_{H_2O_2} + \frac{1}{2}G_{OH}\right) \cdot UO_2(OH)_2\end{aligned} \tag{8}$$

In order to simplify the reaction scheme and the equation, every oxidant has been gathered beyond an operational apparent oxidative specie which is $H_2O_2^*$. By defining

$$H_2O_2^* = G_{HO_2} \cdot HO_2 + G_{HO_2} \cdot H_2O + G_{H_2O_2} \cdot H_2O_2 + G_{OH} \cdot OH \quad (9)$$

It comes out:

$$\left(\frac{3}{2}G_{HO_2} + G_{H_2O_2} + \frac{1}{2}G_{OH}\right) \cdot UO_2 + H_2O_2^* \rightarrow \left(\frac{3}{2}G_{HO_2} + G_{H_2O_2} + \frac{1}{2}G_{OH}\right) \cdot UO_2(OH)_2 \quad (10)$$

Considering the whole mass balance and a given time, the system reacts as if $\left(\frac{3}{2}G_{HO_2} + G_{H_2O_2} + \frac{1}{2}G_{OH}\right)$ moles of UO_2 would be oxidised by one mole of $H_2O_2^*$ producing thus $\left(\frac{3}{2}G_{HO_2} + G_{H_2O_2} + \frac{1}{2}G_{OH}\right)$. moles of $UO_2(OH)_2$. The oxidation rate law of UO_2 can hence be written as

$$\frac{1}{S}\frac{d[U]}{dt}\ (kg\ m^{-2}\ s^{-1}) = \frac{M_U}{\eta}\overline{E}_\alpha \frac{\left(\frac{3}{2}G_{HO_2} + G_{H_2O_2} + \frac{1}{2}G_{OH}\right)}{2} \times \frac{A_v(t)}{N} L, \quad (11)$$

where S stands for the reactive surface area, M_U the molar mass of uranium, E_α the average energy released by spent fuel alpha decays, L for the mean path of α particles in the fuel matrix, G_i for the radiolytic yield of the radiolytic specie i, N is the Avogadro number and η the geometric factor. Reference values of the parameters are given in Table 1.

Using the previous equation and the reference value of the parameters, the fuel corrosion rate R can therefore been expressed as

$$R\ \left(mg\ d^{-1}\right) = 3.86 \times 10^{-15} \cdot S(m^2) \cdot A_v(t)\ \left(Bq\ m^{-3}\right). \quad (12)$$

We hence obtain a relation between the fuel corrosion rate and the reactive surface area and the residual α volume activity of the fuel which can be directly related to the burnup and age of the spent fuel.

3.3. Discussion of the main hypothesis

The Eq. (11) has been derived by using some major hypotheses on the reactivity of radiolytic species at the fuel/water interface, the validity of which is discussed in this section.

- *Diffusion length of α in the UOX matrix* (L)*:* This parameter has been assessed by using the TRIM code [36] based on the Bethe–Bloch equation. No model-specific uncertainty is associated to this parameter but experiments show that penetration depth can deviate roughly 10% from the calculated value.
- *Average energy of α particles* (E_α)*:* The value used for this parameter corresponds to the initial average energy of α particles. More detailed calculations should consider the time evolution of this average energy, but the effect is expected to be of the second order.
- *Geometrical factor* η*:* This parameter is calculated by assessing the solid angle in which a particle has to be to reach the surface assuming it does not loose part of its energy along its trajectory. The value used in the model ($\eta = 4$) is clearly conservative since it assumes that no energy is given to the fuel although the energy loss occurs all along the particle pathway. More detailed calculations showed that most of the release energy comes from the atoms near the surface which do not give much of their energy to the matrix. These calculations also show that η has to be between 4 and 5. Beyond these values, this model assumes that the fuel/water interface can be simulated as a 2-D planar surface with 40 μm of free water, which prevents it from being directly applicable to very small particles (high surface area). In particular, this model can not be applied in very dispersed system where grain boundaries are open to water.
- *Primary radiolytic yield of oxidizing radiolytic species:* The model developed only deals with the primary radiolytic yield after 10^{-6} s and neglects the recombination of radiolytic species together. It also neglects the reducing radiolytic species (in particular H_2) which is clearly conservative. Accounting for the complete reaction schemes would require using a short term

Table 1
Reference value for the parameters used in the Eq. (11) to assess the alteration rate of the spent fuel matrix ((*) taken from [54])

Parameters	Meaning	Reference value
M_U	Molar mass of uranium	$0.238\ kg\ mol^{-1}$
$\overline{E}_\alpha$	Average energy released by spent fuel α decay	5.25×10^6 eV particle^{-1}
G_{HO_2}	Radiolytic yield of specie $HO_2^\bullet$	0.22×10^{-2} eV particles^{-1} (*)
$G_{H_2O_2}$	Radiolytic yield of specie H_2O_2	0.985×10^{-2} eV particles^{-1} (*)
G_{OH}	Radiolytic yield of specie $OH^\bullet$	0.24×10^{-2} eV particles^{-1} (*)
L	Mean path of α particles in the fuel matrix	12×10^{-6} m
N	Avogadro number	6.023×10^{23}

kinetic model which does not seem to be reasonable for predicting any long term behavior. In addition, it would require considering the effective influence of every major and minor groundwater component, which is far from the current state of knowledge.

- *Yield of the oxidation reaction:* One of the major hypotheses we used is that the fuel oxidation reaction is complete and consumes all the produced radiolytic oxidants. This hypothesis is not consistent with the scarce experimental results available which rather show that ~5–10% of the radiolytic oxidants effectively oxidize spent fuel [37]. However, in order to ensure the conservatism of the model, a yield of 100% has been used due to the lack of robust data on the influence of aqueous species on the oxidation yield, on the significance of H_2O_2 dismutation reactions and on the lifetime of radicals. More realistic hypothesis should be available in the near-future based on the available experimental programs.

3.4. Comparison with the experimental data

Fuel alteration rates (mg m^{-2} day^{-1}) as predicted by the Eq. (12) have been compared to available experimental data obtained both on irradiated fuels and on α-doped UO_2 as a function of the residual α activity (MBq g^{-1}) (Fig. 3). It has to be mentioned that the comparison was limited by the frequent absence of indications on the α activity in the literature where the dose is preferentially detailed. Also, we voluntarily restrict our comparison to data obtained in deionised water in absence of any other redox sensitive elements which could consume part of the oxidants and hence decrease the global alteration rate.

From this figure, it can clearly be observed that the model well predicts the evolution of the alteration rate with the residual α activity since the trend depicted by the experimental results is well reproduced. However, the model over-predicts the alteration rate by less than one order of magnitude. This result is not surprising with regards to the numerous conservative assumptions used in the model, in particular about the yield of uranium oxidation by radiolytic oxidants. Interestingly, one can estimate a kind of global effectiveness of the radiolytic oxidants by introducing an effective oxidation yield in the equation and fitting it to the experimental data. This fit is represented on the figure by the dashed line and corresponds to an effective efficiency of 25%. This means that in order to reproduce the experimental data, one has to assume that roughly one eighth of the oxidants effectively oxidize the fuel matrix instead of one half. This value is relatively close to the available experimental values which are rather in the range 5–10%. For the perspective of assessing the global spent fuel performance in geological disposal, this conservative performance was estimated as reasonably good with regards to the robustness of the approach, and it allows overcoming the current uncertainties on the fuel radiolytic alteration.

4. Assessment of the global fuel performance in geological disposal

RN release in geological disposal proceeds by two complementary processes, which are the instantaneous release of the so-called IRF and the continuous but slow matrix release due to the radiolytic dissolution.

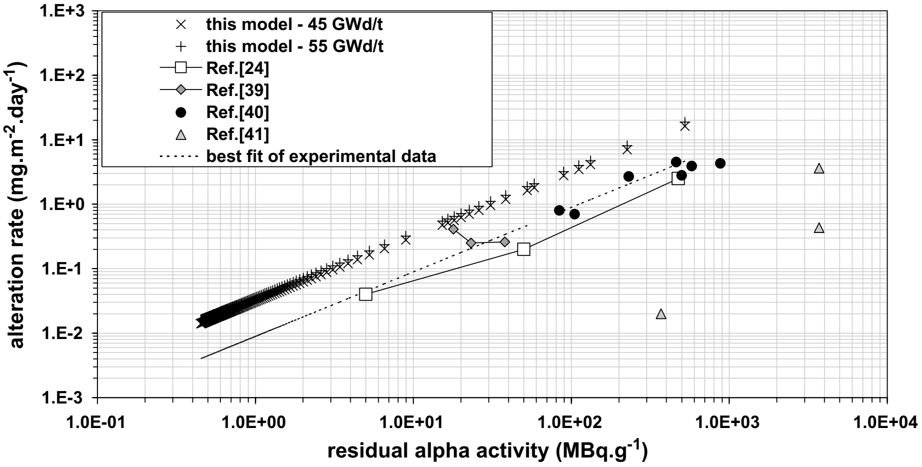

Fig. 3. Comparison of the experimental and modeled alteration rates (mg m^{-2} d^{-1}) as a function of residual α activity (MBq g^{-1}). Experimental data are taken from [24,38–40].

4.1. Assessment of the IRF contribution

The first part of this paper allows proposing a common referential for assessing the IRF inventory as a function of burnup and time [13]. However, some options are still left open to the end-user depending on the anticipated evolution and performance of the fuel matrix. Assessing the global performance of spent fuel therefore requires one to allocate performance to the various fuel microstructures.

Consistent with the approaches chosen for the matrix model, we obviously chose to consider a model integrating all the current knowledge uncertainties and standing on the conservative side. In particular, we consider the potential uncertainties:

- Grain boundaries have been demonstrated to be closed after irradiation if we refer to the relatively slight fission gases release although they have been significantly modified during irradiation: presence of secondary metallic phases, presence of fission gases micro-bubbles which have been demonstrated to be over-pressurized [41],... However, demonstrating their long term stability is not so straightforward. In particular, significant volume of helium is produced within the fuel pellet due to α decay and may progressively migrate towards the grain boundaries [42,43] and precipitate in micro-bubbles which will contribute to decrease the mechanical tightness of grain boundaries. In addition, irradiation defects will accumulate in fuel pellets and may also migrate towards grain boundaries which would also act as defects well. In order to be conservative, we therefore assume in a first approximation that grain boundaries may be permeable to water and slightly open [44]. They can therefore act as a preferential migration path.
- The instability of grain boundaries leads to significant consequences for restructured zones in high burnup and MOX fuels. These zones are the rim zone in the UOX fuels and the large Pu-rich agglomerate in MOX fuels [13]. Indeed, these zones present a high porosity (∼15%) with large pores (1–2 μm) but very small grains (∼0.1 μm). In addition, pores are initially over-pressured. We therefore consider the numerous grain boundaries of the restructured zones as non-confining for assessing the RN release.
- Accumulation of irradiation defects may contribute to the occurrence of α self irradiation enhanced diffusion within the pellet [13,45–48]. This may contribute to the modification of the RN distribution within the pellet and enhance the release of RN to the grain boundaries. Upper boundary diffusion coefficient is estimated to be related to the α residual activity $A_v(t)$ by the following equation [46]:

$$D_{\mathrm{ASIED}}(t) = 2 \times 10^{-41} \cdot A_v(t) \ \left(\mathrm{Bq\,m^{-3}}\right). \tag{13}$$

Considering these uncertainties, we therefore do not allocate any barrier performance to the gap, the grain boundaries and the restructured zone (rim zone in UOX fuel and large Pu-rich agglomerate in MOX fuel, and we estimate that the radionuclides that are present within theses zones as a function of time may be instantaneously released when confinement is breached. We also consider the potential diffusion of radionuclides from the grains (a confining structure) to the grain boundaries (a non-confining structure) due to α self-irradiation enhanced diffusion [49]. Tables 2 and 3 illustrate the assessment of the IRF as a function of time respectively for a UOX and MOX reference fuel of 55 GWd t^{-1}.

Values for MOX fuel are significantly higher than for UOX fuel due to the large contribution of Pu-rich agglomerates which are considered in this first model as non-confining, which is obviously quite conservative.

Table 2
IRF estimates (% of total inventory) for various radionuclides for PWR UO_2 fuel, assuming IRF comprises gap, grain boundaries and all fission products in rim region (grains plus pores)

BURNUP RN	37 IRF	41 IRF	48 IRF	60 IRF	75 IRF
Fission gas	2 (2)	2 (3)	4 (6)	10 (15)	18 (26)
^{14}C*	10	10	10	10	10
^{36}Cl	5	5	10	16	26
^{79}Se	1 (1)	1 (2)	3 (4)	6 (10)	11 (17)
^{90}Sr	1 (1)	1 (2)	3 (4)	6 (10)	11 (17)
^{99}Tc	1 (1)	1 (2)	3 (4)	6 (10)	11 (17)
^{107}Pd	1 (1)	1 (2)	3 (4)	6 (10)	11 (17)
^{126}Sn	1 (1)	1 (2)	3 (4)	6 (10)	11 (17)
^{129}I	3 (3)	3 (3)	4 (6)	10 (15)	18 (26)
^{135}Cs	2 (2)	2 (2)	4 (6)	10 (15)	18 (26)
^{137}Cs	2 (2)	2 (2)	4 (6)	10 (15)	18 (26)

Best estimate values, with post estimate values in brackets (taken from [13]).

Table 3
Distribution of the fission gas in MOX fuel for various burnups (BU); best estimate and pessimistic values (taken from [13])

BU (GWd t_{iHM}^{-1})		40	45	55	60
Gap (%)	Average	2	3.2	5.6	6.8
	Pessimistic	3.8	7.0	13.4	16.6
Restructured Pu rich agglomerates (%)	Average	25	30	30	35
	Pessimistic	50	50	50	50
IIRF estimates	Best estimate	27	33	36	42
	Pessimistic estimate	54	57	63	67

Future models will require the assessment of the Pu-rich agglomerate properties as a function of the radial position in the fuel pellet. Allocating confining properties to the agglomerates seems indeed more realistic for most of the internal agglomerates than for the external ones.

4.2. Assessment of the matrix performance

Eq. (12) relates the RN release from the fuel matrix to the residual α activity and the reactive surface area. It is therefore of prime importance of assessing the global evolution of the spent fuel reactive surface area as a function of time.

4.2.1. Assessment of the relevant reactive surface area of spent fuel

Reactive surface area plays a major role in assessing the fuel performance as evidenced by Eq. (12). However, assessing the long term reactive fuel surface area is quite a challenging task. Indeed, the scarce experimental data on young irradiated fuels indicates that fuel surface area is quite variable, values ranging from 2×10^{-4} to $0.3\,\mathrm{m^2\,g^{-1}}$ [50–53] for burnup comprised between 30 and $60\,\mathrm{GWd\,t^{-1}}$. No clear relation between burnup and surface area is observed. Values rather depend on the nature and size of the samples (powder, pellets) as shown in Fig. 4. In addition, measurements on non-irradiated pellet show that a rugosity factor of $\varepsilon \sim 3$ has to be accounted for. The rugosity factor is defined as the ratio of the geometric to measured surface for a single fragment (or pellet if it is not fractured). After irradiation, a single spent fuel pellet is broken into roughly 15 fragments due to the fractures produced by the thermal gradient during the first and second cycles of irradiation. We define the fracturation ratio, τ, as the average number of fragments per pellet. From these results, reactive surface area of irradiated fuel pellet can be estimated using the following equation:

$$S_{\mathrm{actual}} = \varepsilon \cdot \tau \cdot S_{\mathrm{geometric}}, \tag{14}$$

ε is assumed not to change significantly with time. On the other hand, τ can significantly increase if the grain boundaries are not stable and slightly open with time. However, no model is currently available to describe this evolution. In addition, it is not clear whether any opening of the grain boundaries will actually lead to an increase of the reactive surface area and alteration rate if the grains boundaries are not large enough to allow α particles to produce significant amount of radiolytic species.

4.2.2. Matrix performance

Fig. 5 presents the fuel alteration rate expressed in fraction by year for four different values of the fracturation ratio τ ranging from 15 to 60. With this model, fuel

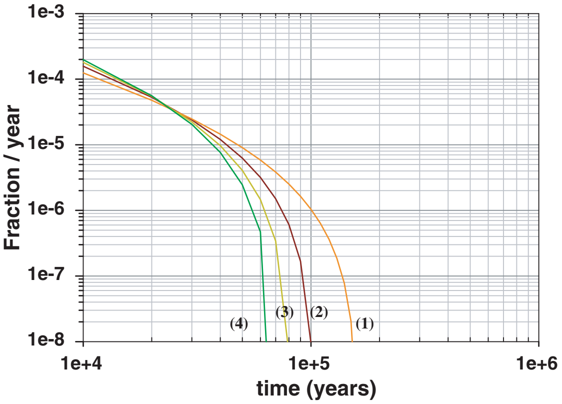

Fig. 5. Fuel performance expressed in fraction released/year as a function of time and fracturation ratio.

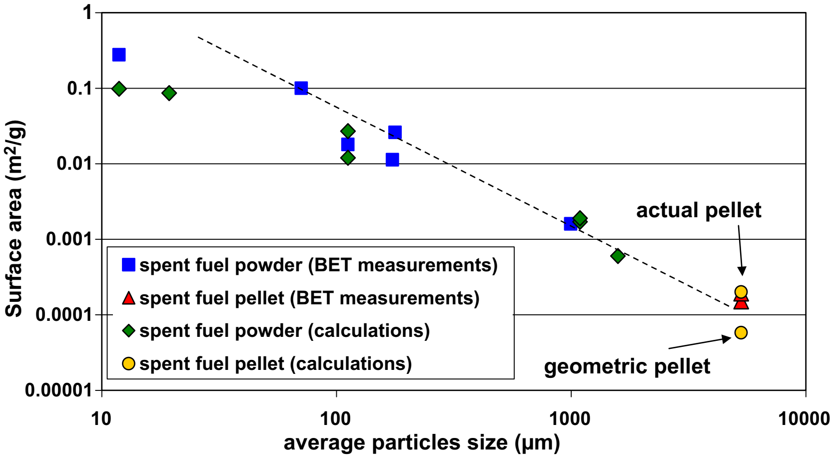

Fig. 4. Relation between the measured or calculated surface area and the average particles sizes for spent fuel for various types samples: powder and pellets.

lifetime is around 10^5 years depending on the reactive surface area. This model can not be extrapolated to high surface area due to the strong assumption concerning the geometry of the fuel/water interface (see previous section).

5. Conclusions

Based on the available knowledge in the literature, a conservative source term has been specifically developed for the performance assessment and safety analyses. It aims to give the bounding values for the RN release from spent fuel while integrating all the current knowledge uncertainties on the fuel evolution and the subsequent performance. In this sense, it has to be distinguished from the more scientific models which aim to integrate and reproduce more precisely all the processes involved in the fuel alteration.

The structure of the IRF model has been described in the first part of this paper [13] and conservative values have been here selected. Concerning the matrix performance, it has been assessed by developing a conservative model for the α radiolytic dissolution. This model is based on some conservative assumptions which were used to overcome the current knowledge and parameters uncertainties, in particular on the detailed radiolytic scheme and the coupling with the environment. This model over-predicts by roughly one order of magnitude the available experimental results in the literature. It also evidences the major influence of the reactive surface area which is a direct parameter influencing the alteration rate. Any evolution of the reactive surface area prior to the water access within the waste package will therefore directly modify the subsequent alteration rate.

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