

# Long term evolution of spent nuclear fuel in long term storage or geological disposal. New findings from the French PRECCI R&D program and implications for the definition of the RN source term in geological repository

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This paper aims to give a brief overview of the wide research undertaken in France in order to elucidate the potential long term evolution of spent nuclear fuels in long term storage or geological disposal. Scientific key issues related to the potential long term evolution in closed system, in presence of and oxidative phase and in presence of water are presented as well as the anticipated trends. A particular emphasis is put on the major outcomes of this research which is a new definition of the radionuclides source term for the geological disposal: we estimate that we have now to allocate a higher fraction of the radionuclides inventory to the so-called instant release fraction which is instantaneously released in presence of water.

**KEYWORDS:** *spent nuclear fuel, long term storage, geological disposal, long term behaviour, nuclear waste*

## I. Introduction

Only two third of the French nuclear fuel annual budget is currently reprocessed in order to balance the mass of Pu produced by reprocessing and that consumed by recycling. Roughly 350 tHM/year are currently stored waiting for further decision which can be either reprocessing, or long term storage or ultimate disposal. It is therefore of major importance to know how spent nuclear fuel can potentially evolve with time in various conditions in order to help the stacking holders in deciding the spent fuel long term management policy. CEA and EDF launched in 1998 a wide joint research program, entitled PRECCI "Programme de Recherche sur l'Evolution à long terme des Colis de Combustibles Irradiés" <sup>1) 2) 3)</sup>, dealing with the long term evolution of spent nuclear fuel in all types of scenarios relevant for the back-end of the fuel cycle : short term or long term storage in pool or in dry conditions, geological deep disposal. This program is also performed in the framework of the 1991 Law on nuclear waste which has given 15 years to the French re&search before the Parliament decide in 2006 the management option of the nuclear waste <sup>4)</sup>.

The aim of this presentation is (i) to give an overview of the status of the French program 2 ½ years after its launching, (ii) to enlighten what are really the most crucial evolution mechanisms which can significantly affect the chemical and physical state of the spent nuclear fuel so that the allocated functions or performances are altered, (iii) to present the new approach we are following for defining the RN source term for geological disposal.

The PRECCI program has been structured around generic operational questions which are related to the scientific requirement of the industrials

in charge of designing long term storage or disposal facilities<sup>1)</sup>. Indeed, to meet these requirements, R&D needs to bring technical and scientific knowledge to predict the coupled evolution with time of the major parameters related to the physical and chemical state of UOX and MOX fuels, as fracture network, surface area, internal pressure, RN inventories and locations, RN release rate ...). The guideline in this program is to separate the potential evolution as a function of the various boundary conditions which can occur in nominal or altered scenarios. On the one hand, in dry interim storage, spent nuclear fuel is expected to undergo an "intrinsic" evolution in closed system, *i.e.* without any exchange of matter with the external medium. On the other hand, spent fuel can be submitted in altered scenario to alteration by the external fluid, either gases or water. In both cases, physical and chemical alteration mechanisms as well as potential source terms have to be defined. Several sub-programs have therefore been identified, the status of some of which will be presented successively in this paper :

- the evolution of the spent nuclear fuel inventories
- the evolution of spent nuclear fuel in closed system including the assessment of the long term mechanical properties of the cladding
- the evolution of spent nuclear fuel in contact with gaseous media (open system) which will not be presented here.
- the evolution of spent nuclear fuel in contact with aqueous media (open system)

## II. Evolution of the spent nuclear fuel inventories.

Predicting the evolution of the spent nuclear fuel inventories is a quite straightforward process since it only results from the decay of the inventory after

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irradiation. However, only the inventories of the relevant elements for neutronics (basically the actinides) or for the credit burn-up have been already qualified by comparison to dedicated measurements on irradiated assemblies: uncertainties range within 5% around the calculated inventories for these elements<sup>3)5)</sup>.

For the other radionuclides, in particular the long-lived fission products, no data are available to assess the uncertainties associated to their inventories. However, the long term impact of some RN like  $^{129}\text{I}$  is directly related to the initial inventory since it is very mobile and does not undergo (at least in a first approximation) any chemical reactions in the geological medium. Knowing more accurately the initial inventory is therefore essential to assess the robustness of the long term radiotoxicity of such elements. In order to overcome this lack of knowledge, CEA and its French industrial partners are currently supporting dissolution experiments of spent fuels to qualify the inventories of the most relevant long-lived RN in representative spent nuclear fuel assemblies. Effort will be focused on  $^{14}\text{C}$ ,  $^{36}\text{Cl}$ ,  $^{93}\text{Mo}$ ,  $^{59}\text{Ni}$ ,  $^{79}\text{Se}$ ,  $^{129}\text{I}$ ,  $^{107}\text{Pd}$ ,  $^{94}\text{Nb}$ ,  $^{93\text{m}}\text{Nb}$ ,  $^{126}\text{Sn}$ ,  $^{90}\text{Sr}$ ,  $^{93}\text{Zr}$ . These qualifications will also require for some of these elements like  $^{129}\text{I}$  or  $^{14}\text{C}$  some experimental and analytical development which are currently on-going since they are partially volatile.

### III. Intrinsic evolution of the spent nuclear fuel in closed system.

During the first stage of evolution, *i.e.* in long term storage and first stages of geological disposal (before site resaturation and canister corrosion), spent nuclear fuel will undergo significant intrinsic evolution in closed system which will modify the known physical and chemical states of spent fuel<sup>6)</sup>:

- The radioactive decay will lead (i) to the formation of significant volume of helium within the pellet by the radioactive decay of the alpha emitters, (ii) to the accumulation of irradiation damages within the fuel oxides since temperature is expected not to be high enough to ensure partial or total annealing, (iii) to a slight evolution of the global inventories and potentially the global oxygen potential of the matrix.
- The thermal decay may lead to a modification of the global chemical equilibrium
- The spent fuel chemical, physical and mechanical dis-equilibria after irradiation may progressively be resolved with time due to slow diffusion or strain.

This paper does not intend to give a detailed description of all the relevant mechanisms which can be found in other publications<sup>1)7)8)</sup> but rather to give an overview of the major outcomes.

- We do not anticipate any significant evolution of the global chemical state of the spent fuel after irradiation. Indeed, the global oxygen potential of the fuel is buffered by  $\text{Mo}/\text{MoO}_2$  and should not

evolve significantly although the global inventories will be modified as well as the temperature. Based on our thermodynamic calculations, we now estimate this question not to be crucial for the long term evolution.

- The relatively large volume of helium produced by the  $\alpha$  decay will probably be slightly released with time from the fuel pellet towards the grain boundaries and the free volumes.

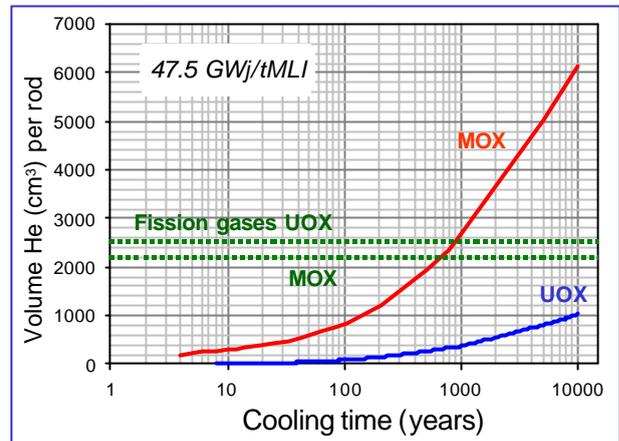


Fig.1: helium volume produced by  $\alpha$  decay in UOX and MOX fuels during the first 10'000 years of evolution.

Ab-initio calculations have been performed and evidenced that (i) He is rather more stable in the U vacancies<sup>9)</sup> (ii) seems not to cause any fuel swelling under the atomic form, and (iii) it probably migrates more quickly than the rare gases. We currently estimate that He will anyway tend to go out of the uranium dioxide and contribute to increase the internal rods pressure. The fate of helium is from our viewpoint one of the major questions addressed by the long term evolution of the fuel.

- Although normal diffusion is probably very low in conditions representative of the back-end of the fuel cycle, we estimate that RN location will evolve with time mainly due to the athermal  $\alpha$  self-irradiation-enhanced diffusion. Based on preliminary assessment<sup>10)</sup>, we estimate that the most mobile elements will slowly migrate towards the grain boundaries which will have to be accounted for when defining the RN source term. It is a major task to quantify the RN irradiation-enhanced diffusion coefficient in  $\text{UO}_2$  matrix and dedicated experiments are currently on-going.
- Finally, the significance of the spent fuel physical state evolution is still to be addressed: can we anticipate a major degradation of the physical state linked to the accumulation of irradiation damages, to the accumulation of microbubbles, to the de-cohesion of the grain boundaries due to ageing ... ? Large-scale integrated experiments

are on-going to evidence the influence of the coupling between all the individual mechanisms on the global evolution of the physical state. The current lack of knowledge on this crucial topic leads us to conservatively assume that the spent fuel physical state is fully degraded when assessing the RN source term<sup>10) 11)</sup>.

- Finally, the Zircaloy-4 cladding will be submitted to a significant hoop stress due to the significant internal pressure: 40 to 60 bars after irradiation, potentially higher with the progressive helium and fission gases release. Consequently, this could lead to a slow creep strain which could potentially lead to failure. Demonstrating the ability of irradiated cladding to accommodate such pressure is necessary before allocating any performance to the cladding. In this context, CEA and EDF research teams are currently developing long term creep model for irradiated cladding and associated rupture criterion<sup>8) 12)</sup> based on experiments conducted on irradiated samples. Basically, no or little creep strain is expected below temperature around 320°C whereas the creep rate then strongly increases with the temperature<sup>7)</sup>. However, the possible occurrence of very slow long term strain at low temperature has to be assessed as well as the influence of the recovery.

From all these results, we anticipate that the physical and chemical state of the spent nuclear fuel will be clearly different after 10'000 y. or more of intrinsic evolution in closed system. The cladding will may have failed according to the temperature level which is related to the selected concept, the pellet integrity can not be ensured and we have to consider the potential loss of cohesion between the grains which could lead to a 8 µm-diameter grains powder instead of a pellet. In addition, the RN location will be different, part of the most mobile RN having migrate towards the grain boundaries by  $\alpha$ -self irradiation induced diffusion processes.

#### IV. Evolution of spent fuel in presence of water.

The major issue concerning the evolution of spent fuel in presence of water is to develop and qualify a robust RN source term which can thereafter be used in performance assessment calculations. A lot of experimental work has already been performed on (i) the determination of the so-called "labile fraction" in leaching experiments on fresh fuel, (ii) the assessment of the corrosion rate for spent fuel in various types of water<sup>13)</sup>. Following the Canadian safety approach, we assume the global RN source term to be composed of two major contributions which are (i) the RN which are instantaneously mobilisable by water when water comes in the canister, the so-called "instant release fraction" (IRF) and the RN which are released through the alteration of the  $\text{UO}_2$  grains, the so-called "matrix fraction". Scientific issues are rather different for these two aspects.

#### 1. matrix fraction : alteration rate of the grains.

One of the major open question is to discriminate the relevant mechanism governing the long term alteration rate for the matrix: either the alteration is driven by the water  $\alpha$  radiolysis at the fuel/water interface, either the alteration is controlled by the solubility, or more probably, the long term rate is a successive combination of both mechanism.

Although much is known on  $\gamma$  radiolysis, very few works focused on the influence of  $\alpha$  particles on aqueous chemistry at the water/solid interface and the influence on the long term alteration rate of spent fuel. In particular, R&D has to assess the relationship between the radiolytic degradation rate and the residual  $\alpha$  dose which will be necessary to assess a potential time-threshold beyond which the alteration could be solubility-controlled. In order to tackle these demanding goals, CEA supports various kinds of experiments: dissolution experiments on  $\alpha$  doped  $\text{UO}_2$  samples, in presence of  $\gamma$  source and simple experiments with  $\alpha$  beam allowing to accurately characterise the involved chemical species. Fuel specific surface area is also a determining parameter in case of  $\alpha$  radiolytic degradation mechanism due to the low penetration depth of  $\alpha$  particles in water (40~µm). This parameter will probably strongly evolve during the first intrinsic evolution in closed system as previously described.

All this mechanistic work will obviously be confronted to the results of dissolution tests performed with actual spent fuel samples<sup>14)</sup>.

#### 2. Instant Release Fraction. (IRF)

Concerning the IRF, we demonstrated that the value derived from experiments on fresh spent fuel are not relevant to assess the long term instant release fraction due to the expected evolution before the access of water<sup>10)</sup>. In order to overcome this difficulty, we developed a new approach which intrinsically accounts for (i) the RN location within the rods after irradiation (grain boundaries, fractures, grains, rim) (ii) its potential evolution with time under the influence of Fickian and irradiation-enhanced diffusion<sup>10)</sup>. In view of the previous evolution in closed system, we chose not to allocate any performance to the RN located in the gap, the rim zones, and the grain boundaries assuming they are instantaneously released when water arrives in contact with. The RN inventories associated to these locations are defined through a stepwise and conservative approach chosen to overcome the current lack of accurate data on the diffusion processes (see §.2). This approach leads to significantly higher IRF inventories: first estimates based on a simplistic hard spheres model lead to 30% IRF at initial time increasing up to 90% after 100'000y for most of the RN<sup>11)</sup>.

With such developments, CEA aims to get a robust and conservative, even if significantly higher than classically assumed, RN source term for geological disposal conditions before 2006. The increase of the instant release fraction which is the major contribution to the radiological impact of spent fuel disposal will therefore have to be accounted for in the designing of the geological disposal. However, we are confident that such approach is the only viable mean to overcome the problem of the spent fuel evolution in the first stages of geological repository and in addition, to intrinsically account for the current and future evolution of spent fuel characteristics (enrichment, burnup ...). All these data will provide reliable and necessary tools to assess the long term impact of the various spent fuel management option and will help stacking holders to draw a possible best scenario to manage spent nuclear fuel among long term storage, final disposal and processing processes options.

## V. Conclusions.

CEA is involved together with its industrial French partner EDF and partially FRAMATOME and COGEMA in a large scale R&D program dealing with the long term evolution of spent nuclear fuel in long term dry storage and in geological disposal. The aim of the French program on spent fuel long term evolution is thus to completely and accurately study the potential evolution mechanisms in the various representative boundary conditions for the back-end of the fuel cycle. We aim to be able to qualify and quantify all the relevant evolution mechanisms so that the most significant one can be determined and accounted for in the development of operational models. These operational models will allow to predict the evolution of a given function (confinement, recovery ...) in a given scenario and will therefore help to design the storage or repository facilities.

First robust and conservative RN source terms for geological disposal and long term dry storage are currently under assessment and will soon be accurately published. However, we estimate that some issues are rather new and complexes and will require additional effort. Among these is the evolution of the spent fuel physical state and integrity which is quite a challenging task considering the wide coupling processes occurring.

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