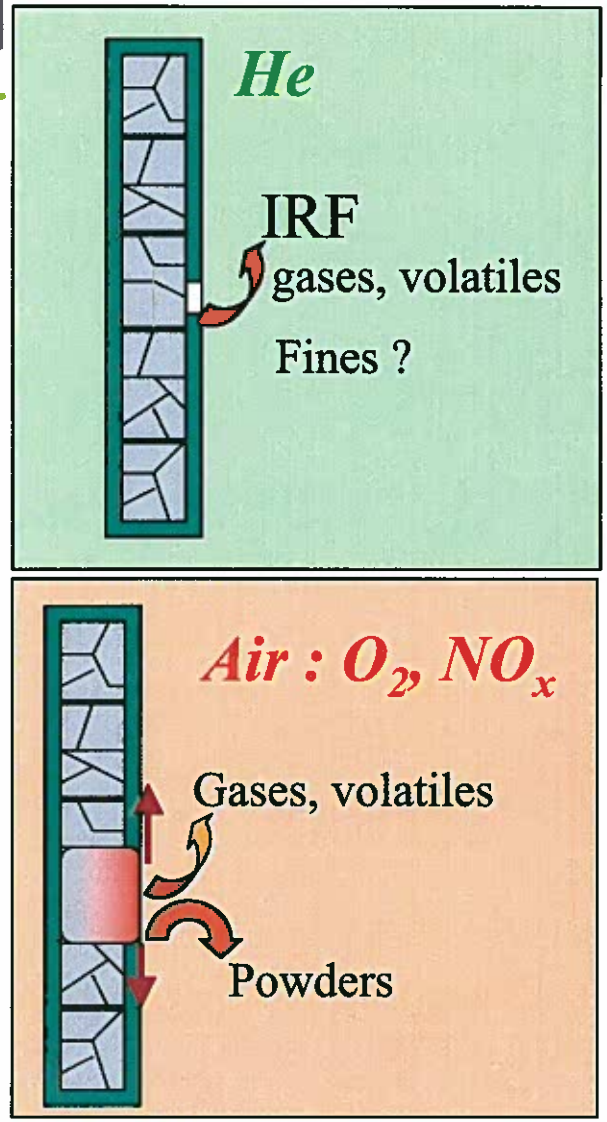
Expected evolution of spent nuclear fuel in long term dry storage. Consequences on the RN source-term models

Cécile Ferry
Christophe Poinssot

INTRODUCTION : General description



Two types of RN release

❑ **« Instant » release of activity at the cladding failure**

IRF Model

❑ **Slow release of activity**

Normal scenario: Evaporation of low volatile species → neglected (confined atmosphere, initial defect in the cladding)

Incidental scenario(rupture of confinement) : Oxidation of UO_2 to U_3O_8, volume swelling ~36%, propagation of the initial defect in the cladding, reduction of the pellet into powder and release of volatile species contained in the grains

No alteration model proposed up today

IRF Model: Instant Release Fraction at the cladding failure

❑ RN release depends on the evolution of the SNF before the cladding failure

Initially out-of-equilibrium : Temperature ↘ and high α and $\beta\gamma$ activities

Evolution of chemical state

Evolution of $\Delta G(O_2)$ due to thermal and radioactive decay has been demonstrated not to be significant !

Evolution of RN location

Migration of RN and He due to temperature and α radiation *not relevant*

Helium fate

Significant He volume produced *Solubility and diffusion properties in spent nuclear fuel indicate precipitation of bubbles in grains in a first step*

Evolution of physical state

No significant effect of irradiation damages on solid swelling
Effect of He bubbles *on LT stability of grain boundaries ?*

IRF Model: Instant Release Fraction at the cladding failure

Context

Dry storage up to 300 y. ⇨ Release in air of gases and vapors

Temperature < 400°C

❑ Based on inventories and chemical form of RN in the spent fuel rod after irradiation

Most volatile potential chemical form (^{14}C, ^{129}I)

⇨Classification of RN as a function of their origin and potential volatility

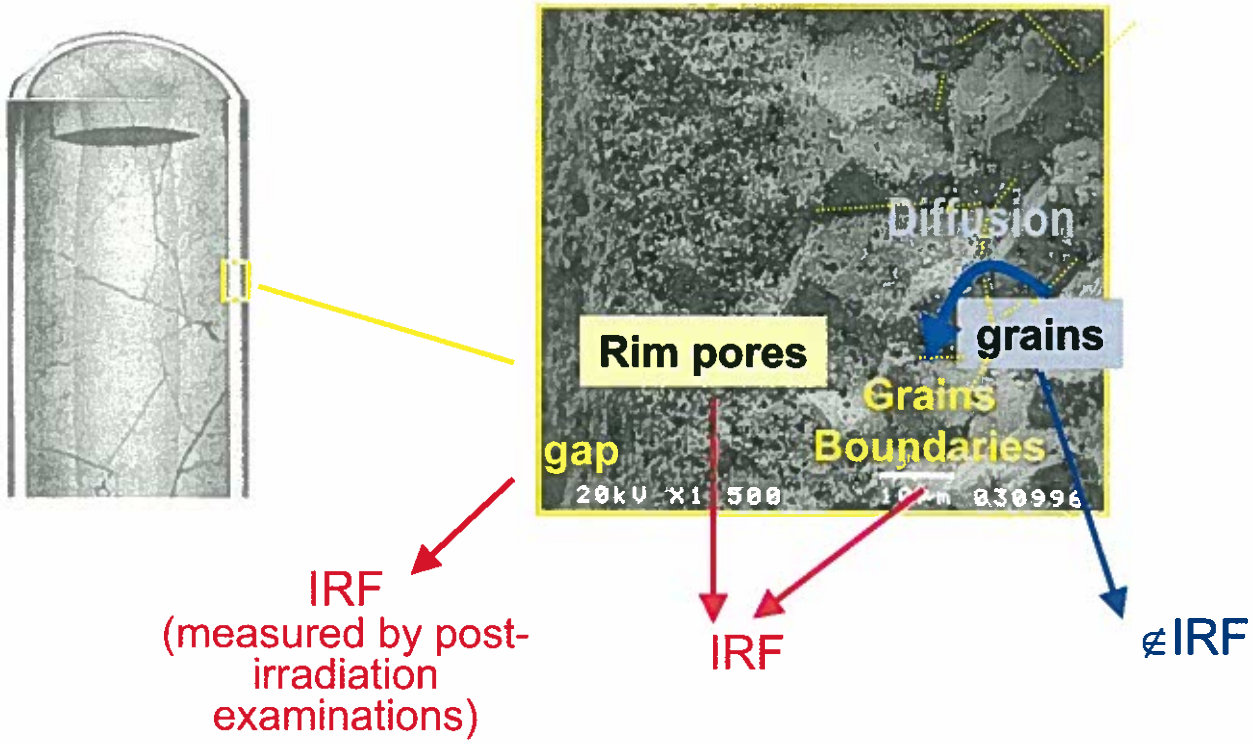
1. **Gaseous** fission or impurity activation products – ^{3}H, ^{85}Kr, ^{36}Cl, potentially under gaseous form– ^{14}C or **high volatile** –^{129}I ⇨ ***IRF(t)- Fraction of inventory located in the spent fuel rod zones with low retention capacity in the LT***

2. **Low volatile** fission products – ^{79}Se, ^{90}Sr, ^{134}Cs, ^{135}Cs, ^{137}Cs ⇨ ***Saturating vapor pressure at equilibrium***

3. U chain **gaseous daughters** –^{220}Rn, ^{222}Rn ⇨ ***Direct recoil + diffusion in pores + gap+ GB***

1.2 IRF Model: Gases and high volatiles (^{3}H, ^{85}Kr, ^{36}Cl, ^{14}C, ^{129}I)

❑ IRF defined as the inventories located within the microstructures with anticipated low confinement properties on the long term

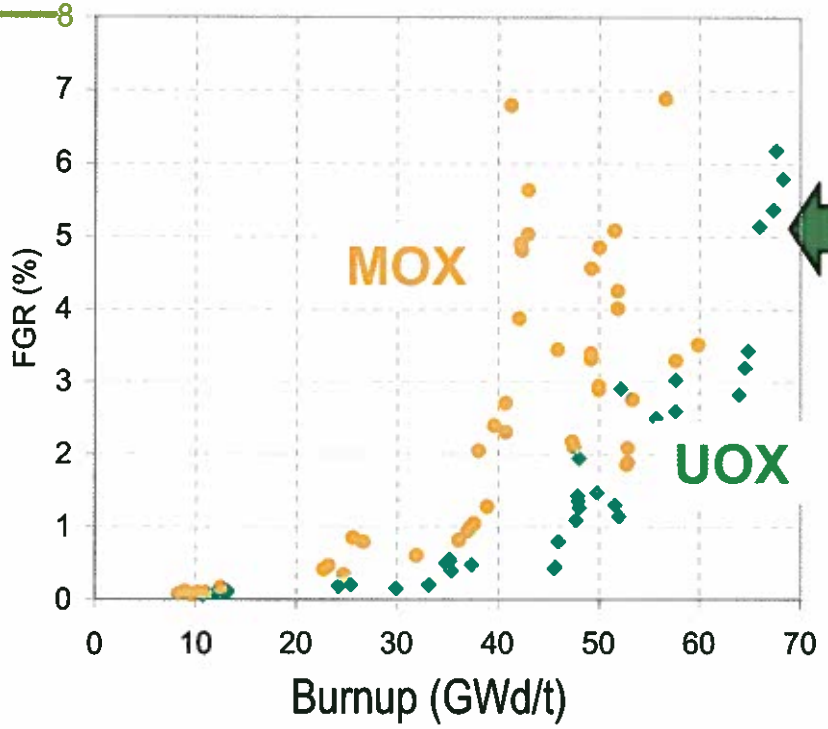


$$IRF(t) = IRF_o + F_{diffusion}(t)$$

Initial data (after irradiation) — Diffusion contribution

1.2 IRF Model (Gases and high volatiles): IRFo

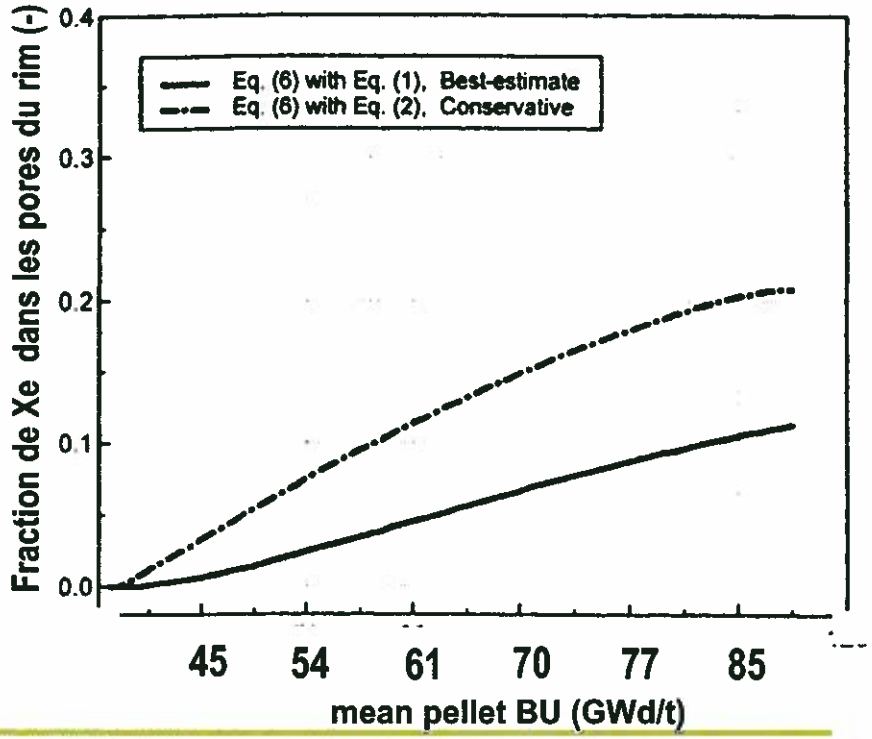
- RN inventories based on distribution of FG in the spent fuel rod



Post-irradiation examinations

Fraction of fission gases released in the free volumes of the rod

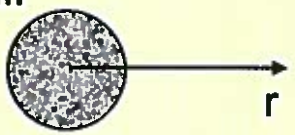
Fraction of FG in rim pores after irradiation



1.3 IRF Model (Gases and high volatiles): $F_{diffusion}(t)$

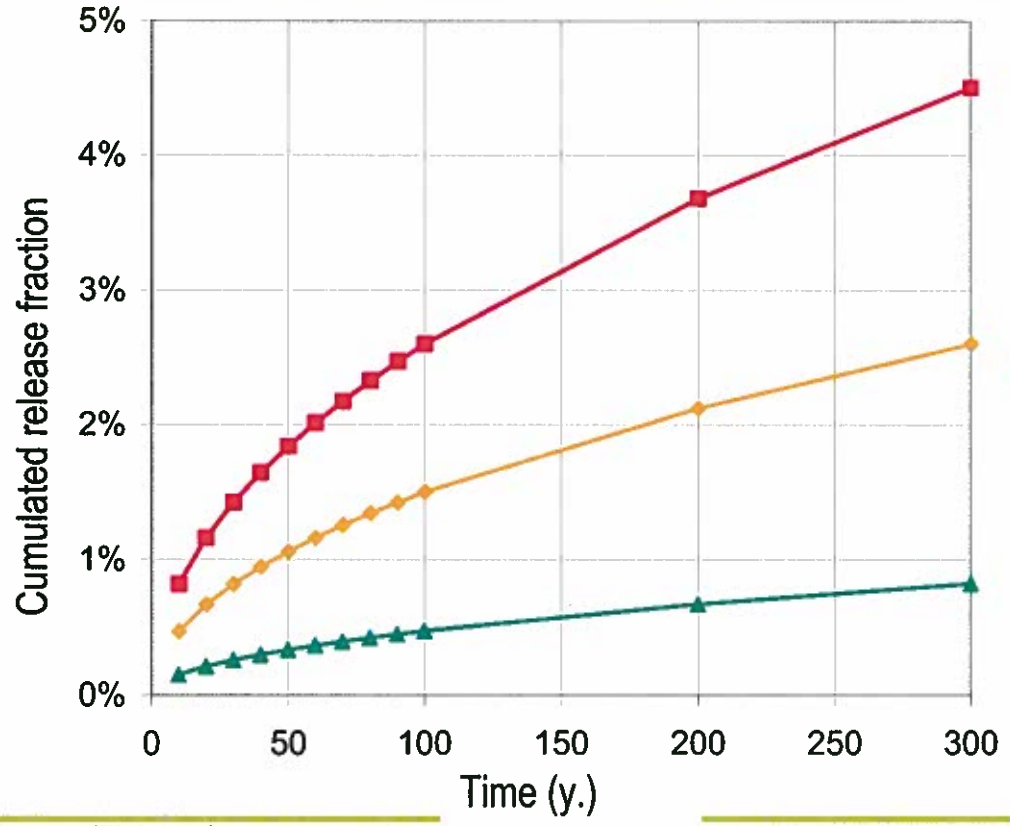
- Fraction released by diffusion from the grains as a function of time

Pellet composed by spherical grains with radius = 4 µm



Diffusion equation

$$\begin{cases} \frac{\partial c}{\partial t} = D(t)\,\Delta c = D(t)\left(\frac{\partial^2 c}{\partial r^2} + \frac{2}{r}\frac{\partial c}{\partial r}\right) \\ C(r=a)=0,\ C(r<a,\ t=0)=C_0 \quad D = 2 \times 10^{-41} \cdot Av \end{cases}$$

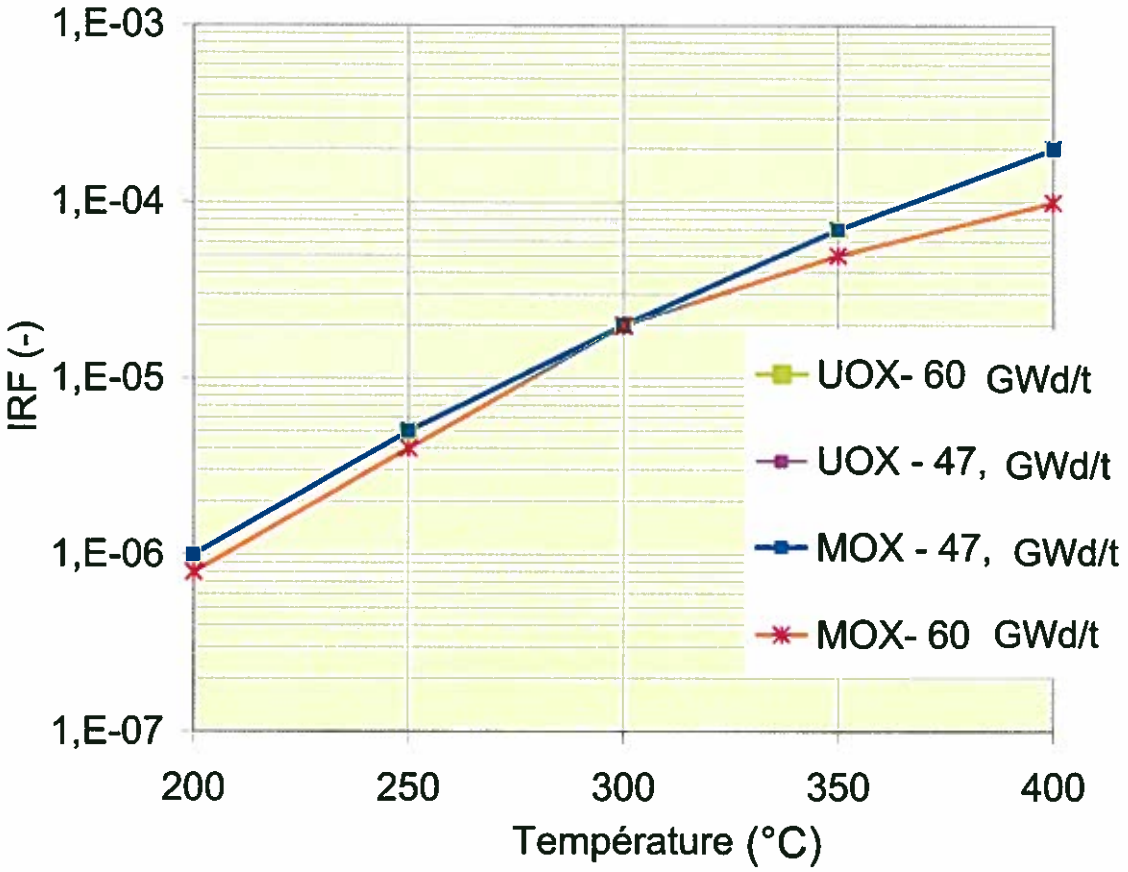


2. IRF Model: Low volatiles (^{79}Se, ^{134}Cs, ^{135}Cs, ^{137}Cs, ^{126}Sn, ^{90}Sr)

$$IRF(t_R) = \frac{A_{rel}(t_R)}{A_{ini}} = F_{vsat} \times e^{-\lambda . t_R}$$

Equilibrium between liquid and gas phase in the rod: **Fraction of saturating vapor** determined from the:

- ⇨ **Saturating vapor pressure**
- ⇨ **free volume** in the rod
- ⇨ **total inventory** of the element in the rod



IRF essentially depends on temperature

3. IRF Model: Gaseous radioactive daughters – ^{220}Rn, ^{222}Rn

$$IRF_{Rn} = \frac{A_{Rn}^{rel}}{A_{Ra}}$$

- Fraction of Rn atoms released by direct recoil and diffusion

- **in gap from a cylinder (diameter = 8 mm)**
- **in grain-boundaries from grains of 8 μm**
- **in pores of restructured zones from grains of 0.1 μm**

4. IRF Model- SUMMARY

IRFo (-) values in dry storage
(no contribution of diffusion, no decay)

	PWR, BU = 55 GWd/t, T = 300°C	PWR, BWR, T = 530°C ??
	This model	*NUREG-1536*
^{3}H	0,01	*0,3*
^{85}Kr	0,07	*0,3*
^{129}I	0,07	*0,1*
^{14}C	0,1	*nd*
^{36}Cl	0,1	*nd*
^{135}Cs, ^{137}Cs	2×10^{-5}	$2,3 \times 10^{-5}$
^{79}Se	7×10^{-5}	*nd*
^{90}Sr	3×10^{-8}	$2,3 \times 10^{-5}$
^{220}Rn, ^{222}Rn	4×10^{-3}	*nd*
^{106}Ru	nd	$1,5 \times 10^{-5}$

5. IRF MODEL: Conclusion

❑ IRF values established

- for each RN of concern as a function of its production mode in the SNF and its volatility
- as a function of burnup

❑ Discussion : Pessimistic assumptions

1. The most volatile chemical form taken into account → ^{14}C, ^{129}I
2. For RN considered as gases or high volatile

   Sum of 2 contributions : IRFo et $F_{diffusion}(t)$

IRFo { Fraction of fission gases* in the free volumes of the rod and in rim pores after irradiation **

Major contribution to IRF(t_R)

$F_{diffusion}(t)$ { Cumulated release by the grains due to alpha enhanced diffusion diffusion with a major value of $D \sim 10^{-25}$ $m^2.s^{-1}$

Contribution not significant

6. Reduction of uncertainties and perspectives

❑ IRF Model

1. Improve chemical characterization of elements in the spent fuel pellets after irradiation ⇨confirm thermo-chemical calculations results

→ Reduce the IRFs of ^{14}C, ^{129}I, Cs

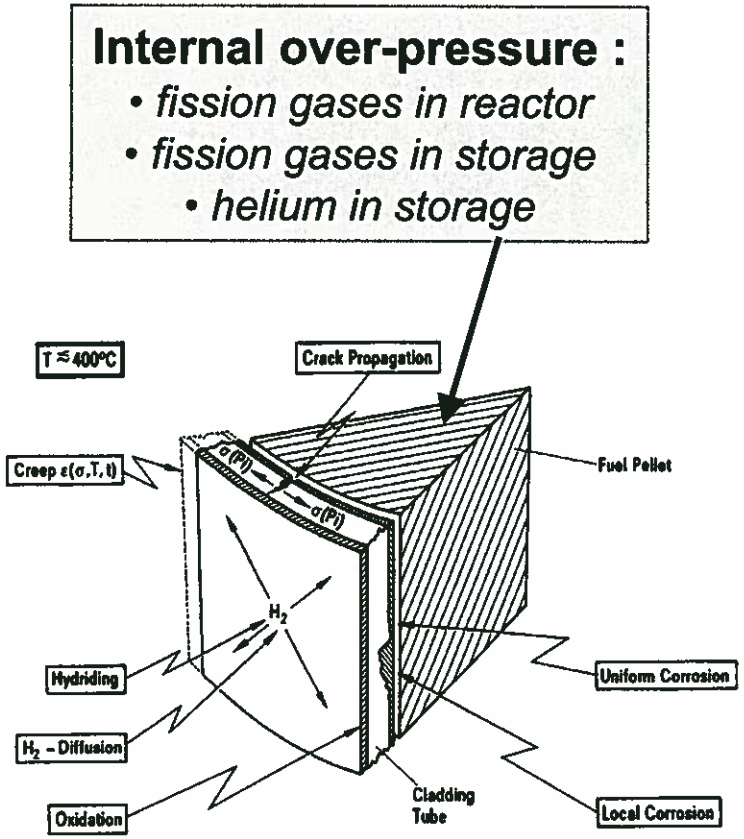
2. Demonstrate the stability of grain boundaries on the period of dry storage ⇘ IRF of gases or high volatiles

3. Quantify the real distribution of the RN of concern in the spent fuel rod through post-irradiation examinations

❑ Incidental scenario: Alteration of a defective spent fuel in oxidative atmosphere

Simplified approach to develop in agreement with the scientific model proposed by the project

Evolution of the irradiated cladding ?



- ***Cladding weakened by irradiation***

  Accumulation of irradiation damage, hydrides, corrosion layer, embrittlement

- ***Main issue = can the cladding be the first confinement barrier in dry storage ?*** Two potentially limiting phenomena

  - ***Creep under internal pressure*** (the main phenomenon potentially leading to rupture in **hot conditions**): Predictive creep model adapted to the long term and rupture criterion

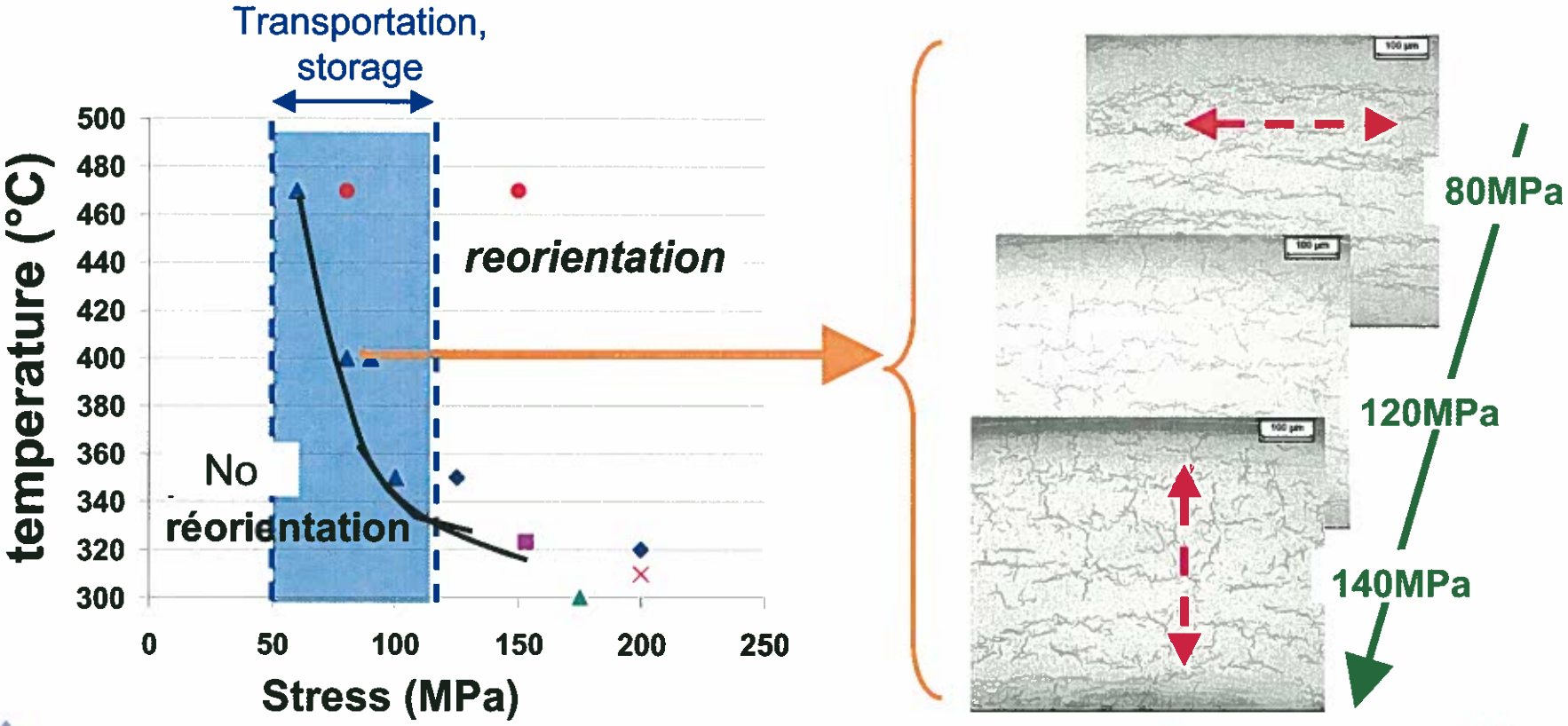
  - ***Hydrides reorientation*** (potential radial orientation of the hydrides **during cooling** under pressure): conditions for reorientation, consequences on the mechanical behavior, in particular during retrieval of the fuel assembly

- ***Development of a stepwise approach***

  From short term experiments and models to longer terms → micro mechanical approach

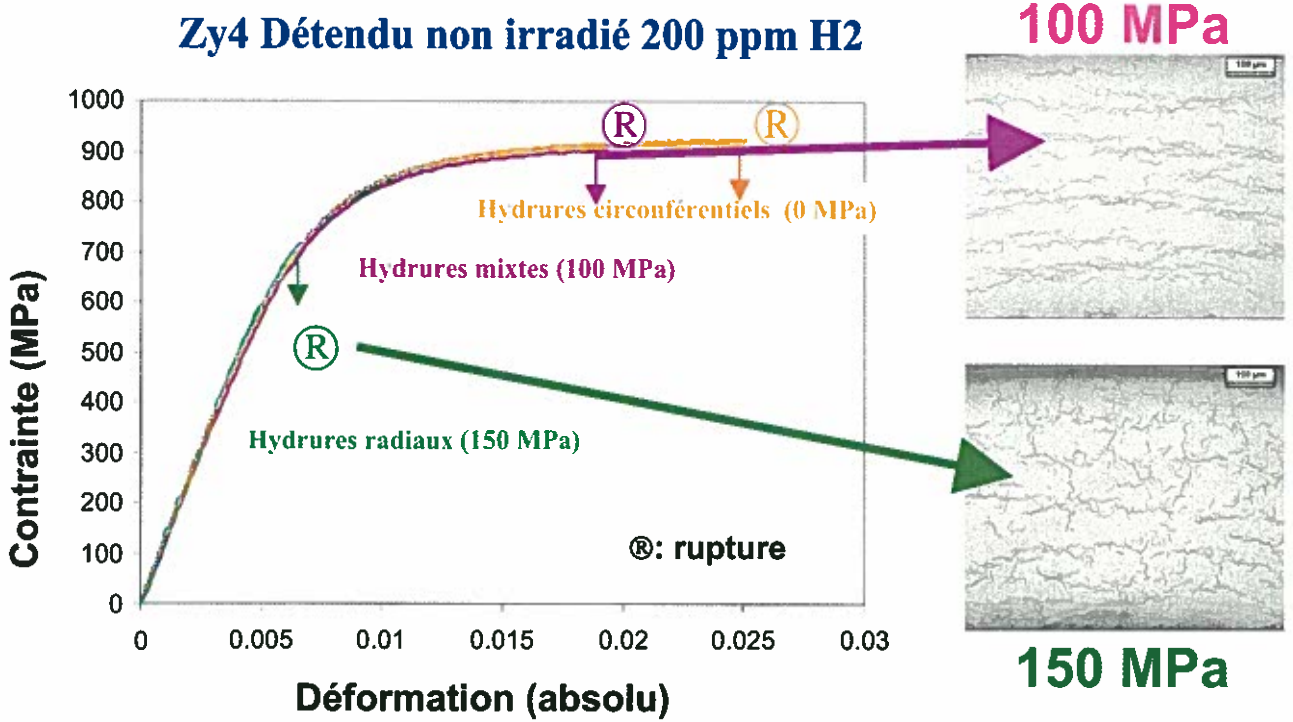
Cladding behavior: Hydrides reorientation during cooling

- During incidental dry transportation (high T°C), fast cooling with a significant stress can lead to hydrides reorientation from tangential to radial mode.
- 1st step: Evaluation of the domain in which the re-orientation is efficient



Influence of hydrides orientation on mechanical properties

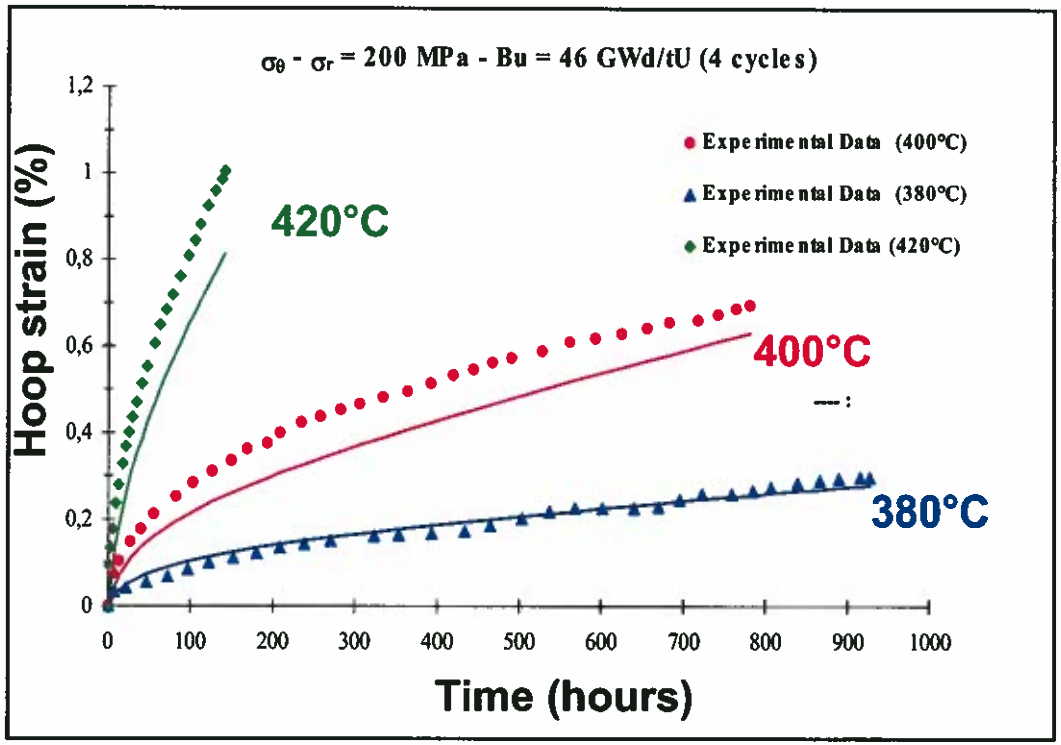
- 2nd step: evaluation of the consequences on cladding mechanical properties.
  - No effect of the hydrides reorientation on the strain rate law
  - Decrease of the strain at rupture with the radial reorientation



Burst test at 20°C → **Risk: cladding rupture facilitated by hydrides reorientation**

Cladding behavior: Long term creep law

❑ From the short term to the long term

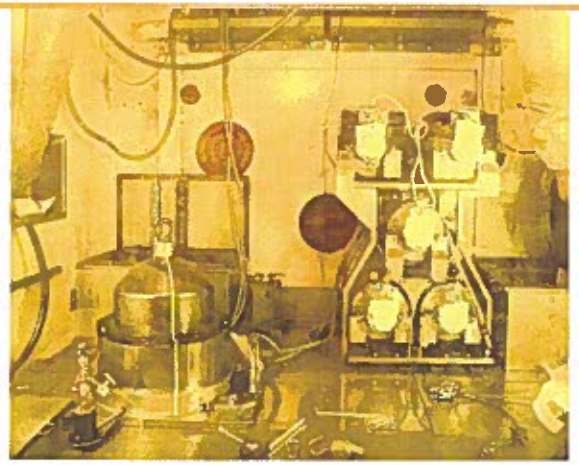


Development of a first model based on a large database of experiments < 60d.

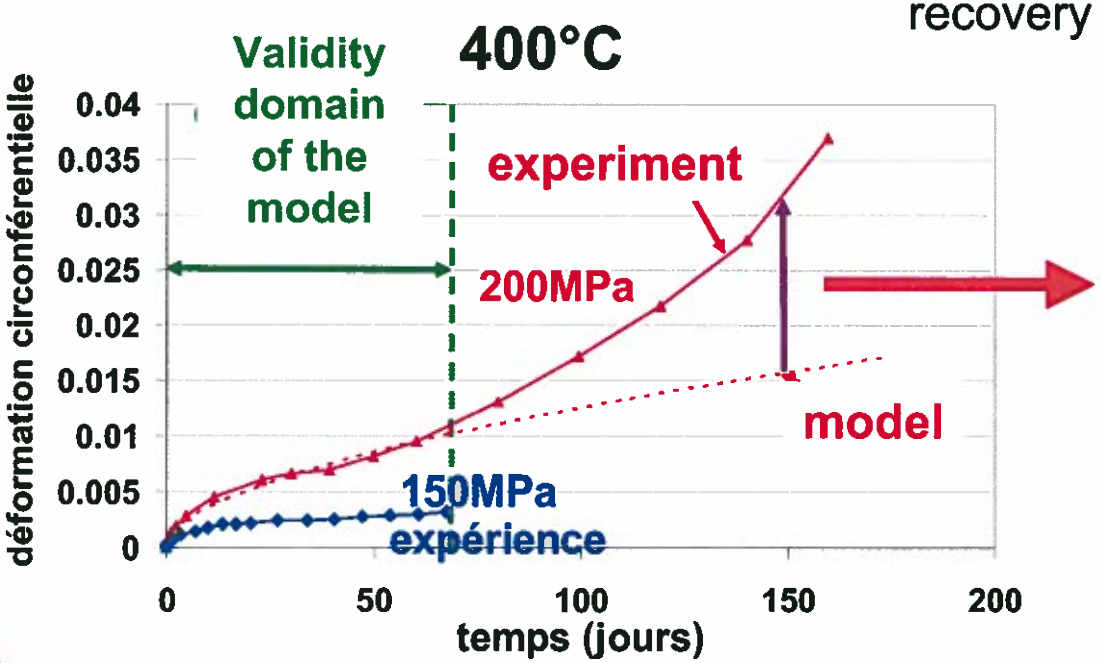
- Good reproductibility of experimental trends and results
- Validation domain: 350-420 °C, 50-200 MPa, up to 60d.

- In parallel, development of long term experiments and microstructural characterization

Cladding behavior: Long term creep law

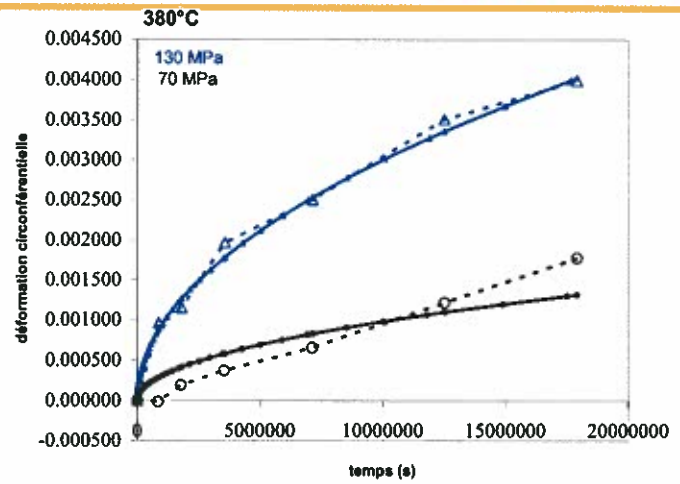


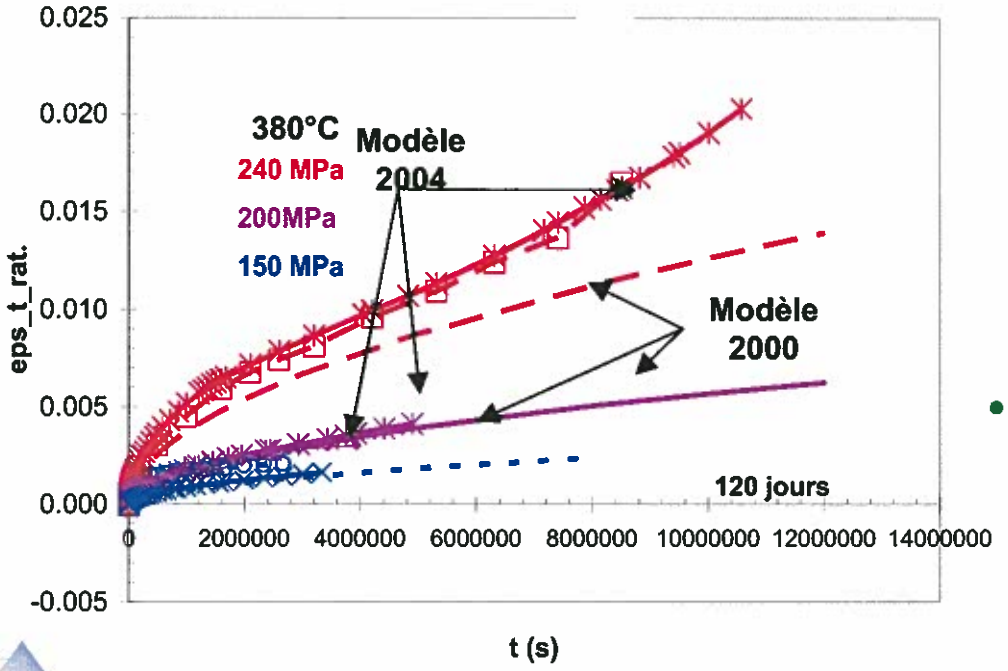
- Development of new mechanical facility in Saclay
  - Long term creep device
- Under-prediction of the first creep model after 60 d.
  - HRTEM characterization evidenced the occurrence of a progressive recovery of irradiated damages



HRTEM observations on strained irradiated samples

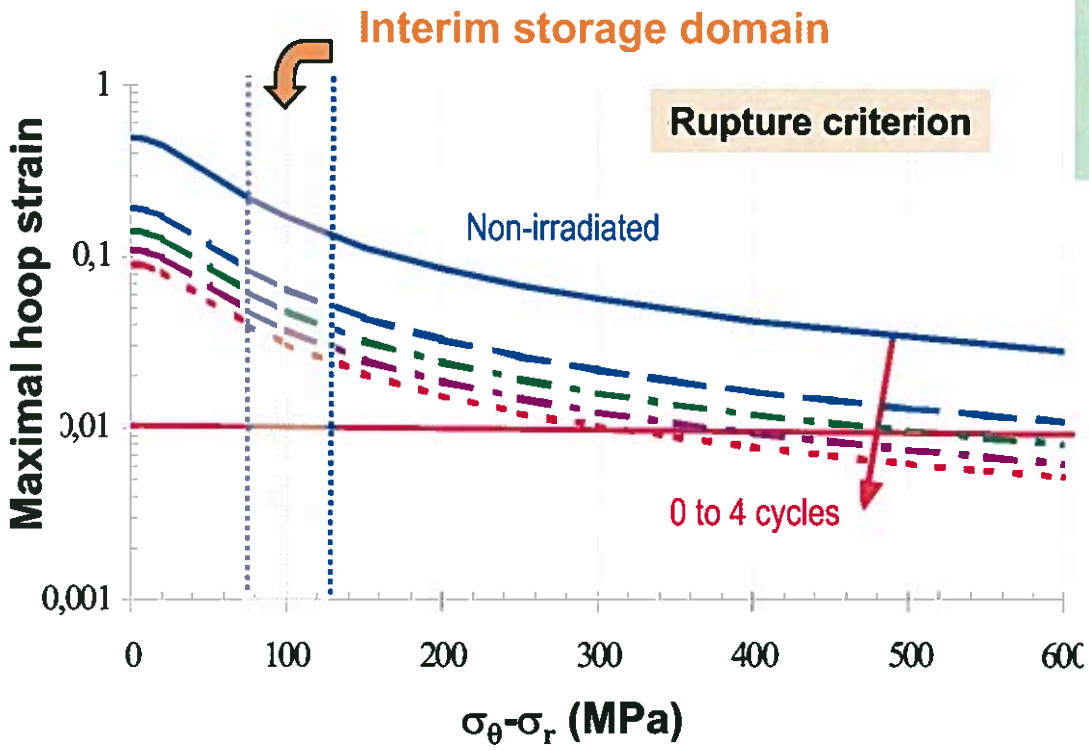
Cladding behavior: Long term creep law





- Development of new creep law integrating the recovery mechanism
  - Enhancement of the validation domain and of the capability to be extrapolated to longer term
    - Integration of the anticipated governing mechanism
  - Better description of the cladding behaviour up to 7 months experiments
- Longer term experiments still ongoing coupled to **micro mechanical** modeling

Cladding behavior: New rupture criterion



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❑ Based on the analysis of the CEA's data on creep rupture of CWSR Zircaloy-4

- Temperature domain: 350 to 470°C
- Stress domain: 100 to 550 MPa
- 0 to 4 cycles

Oxidation of the spent fuel rod

× Oxidation scheme of UO_2

UO_2 → U_4O_9/U_3O_7 → U_3O_8 (swelling (36 %))

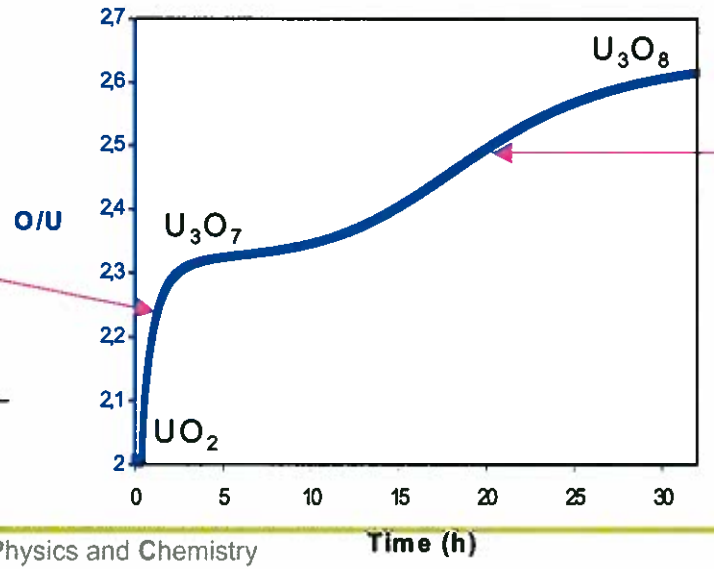
Diffusion process
Ea well known

Germination – growth process
Simplified approach → high variability of Ea !!

- **Most of the kinetic studies use the rate limiting step approximation**:
  - The reaction kinetic is driven by an unique mechanism which imposes its speed to all the other reaction steps
  - The kinetic can be studied on any reaction step. Generally the gas absorption step is characterised with TGA.
- **In the case of the UO_2 oxidation, 2 limiting steps were implicitly proposed**

A diffusion limited oxidation form UO_2 to U_3O_7

$$1-(1-\alpha)^{\frac{1}{3}} = \sqrt{\kappa t}$$



A growth limited oxidation in U_3O_8

$$-\ln(1-\alpha) = (kt)^3$$

Oxidation of the spent fuel rod

Two types of studies

❑ Macroscopic approach on spenf fuel

Weight gains and various characterizations (optical observations, EMPA)

❑ Microscopic approach on UO_2

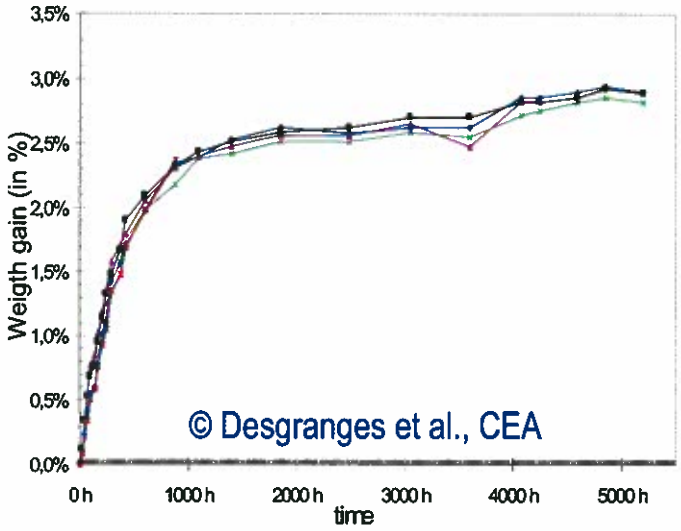
Structural analysis by DRX (*in situ*) and MET

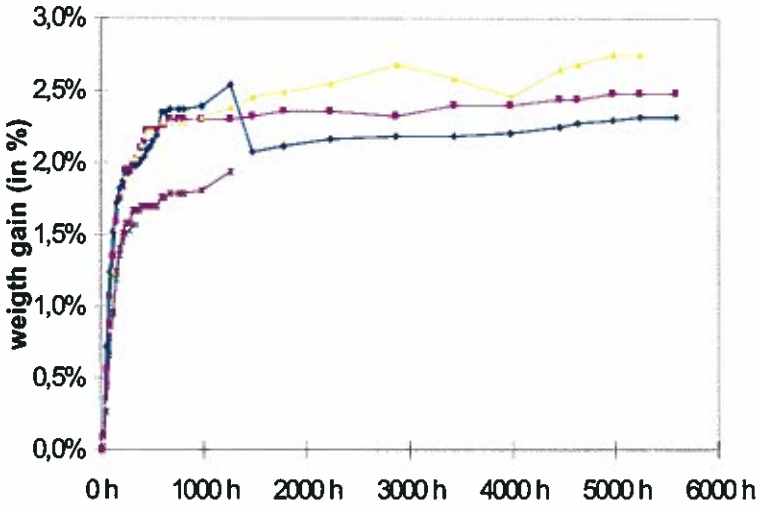
➡ Identification of oxidation mechanisms at microscopic scale to support low temperature extrapolation of kinetic laws

Oxidation of the spent fuel rod

❑ Macroscopic approach on spent fuel

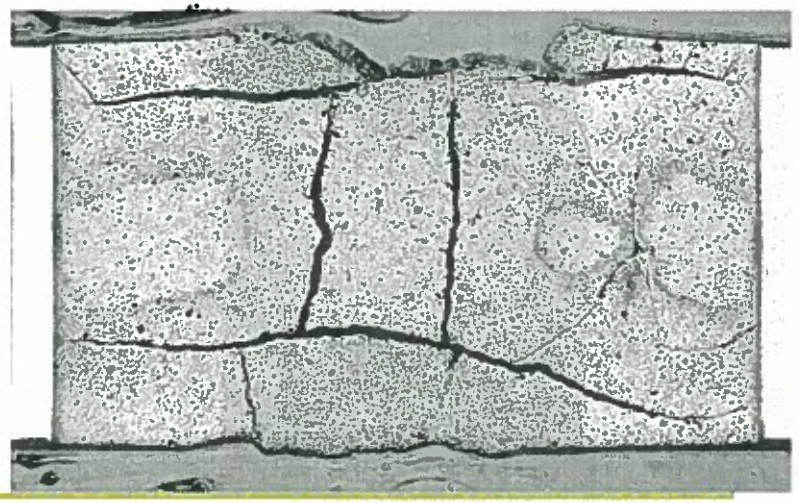
Measured weight gain of UOX and MOX fuels fragments (200 °C, Hr = 30 %)





From UO_2 to U_3O_7

- Increase of the fragment porosity and partial opening of grain boundaries after 875 h of heat treatment in UOX fuel, no RN migration
- Oxidation of MOX faster than UOX but delayed oxidation of Pu rich agglomerates
- Complex oxidation front of the fragment



Oxidation of the spent fuel rod

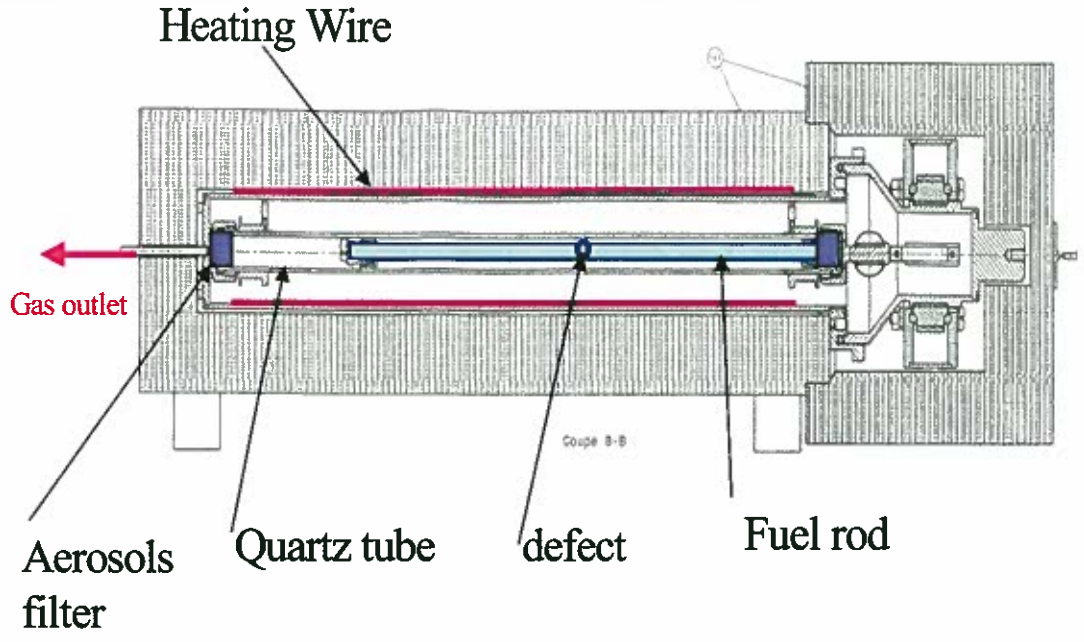
Integrated experiment : Rod alteration in controlled atmosphere

Study of the coupled mechanisms :

- oxidation kinetics
- RN release
- oxygen diffusion in the rod
- cladding deformation and failure propagation

by

measurements of weight gain and cladding deformation, visual observation, gamma scanning.



Development and validation of a RN release model due to alteration of a defective fuel rod in a gaseous phase

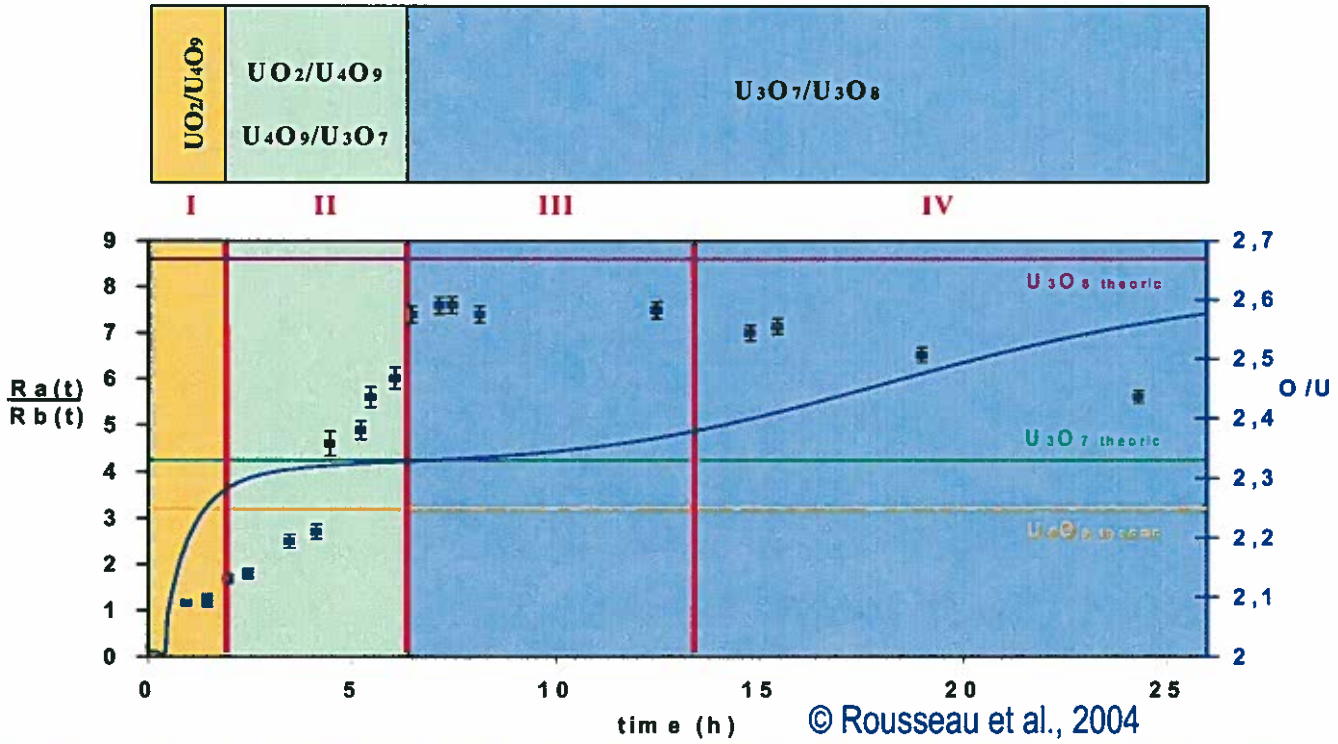
Oxidation of the spent fuel rod

❑ Microscopic approach on unirradiated UO_2

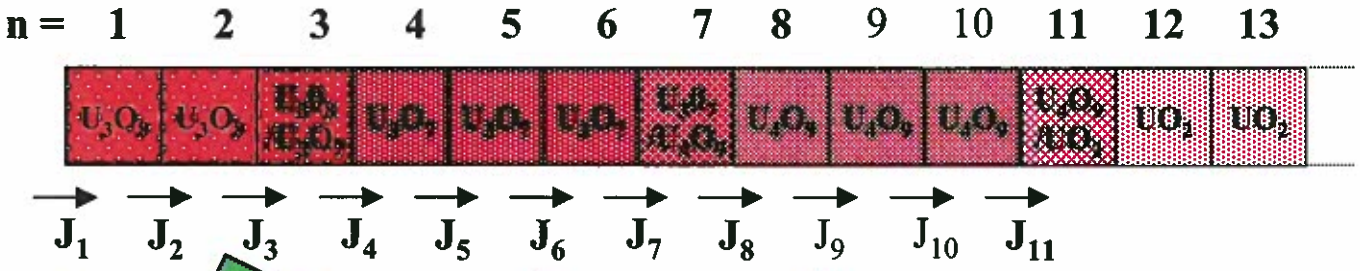
- ESRF X-ray diffraction: Confirmation of the crystalline phase sequence : $UO_2 \rightarrow U_4O_9 \rightarrow U_3O_7 \rightarrow U_3O_8$
- ILL neutron diffraction:
  - Evidence of crystalline relationships between the phases
  - Determination of U_4O_9 crystalline structure

•TGA:

Four domains with different kinetics during oxidation



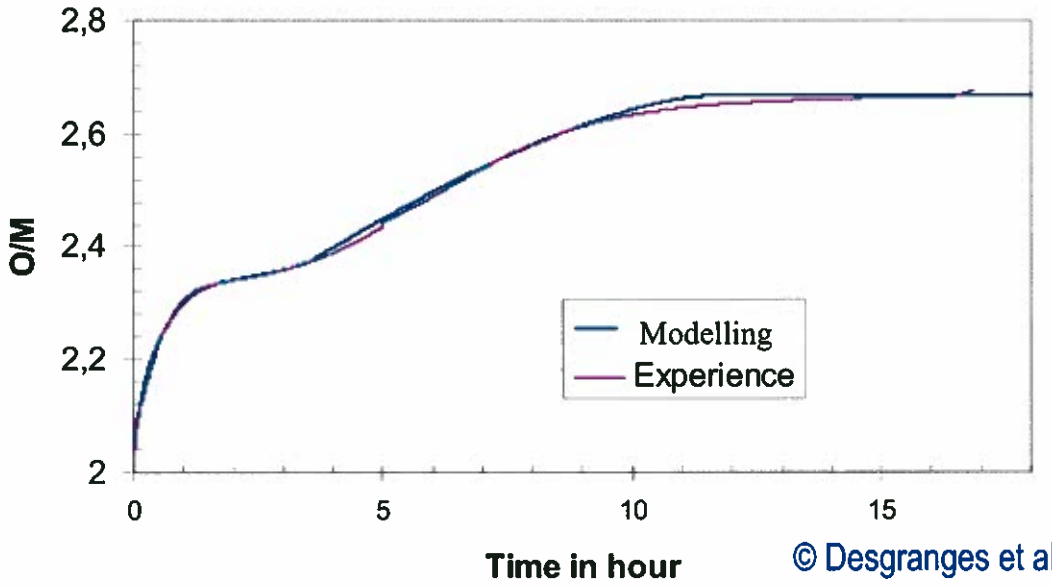
Modeling of the UO_2 grain oxidation



$J_1 = (1-\theta).k_{phase}.A_{atm}$

$$J_n = D_{phase}.\frac{Co_{n-1} - Co_n}{e}$$

Finite difference modeling taking into account 4 phases, which allows the prediction of the plateau



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