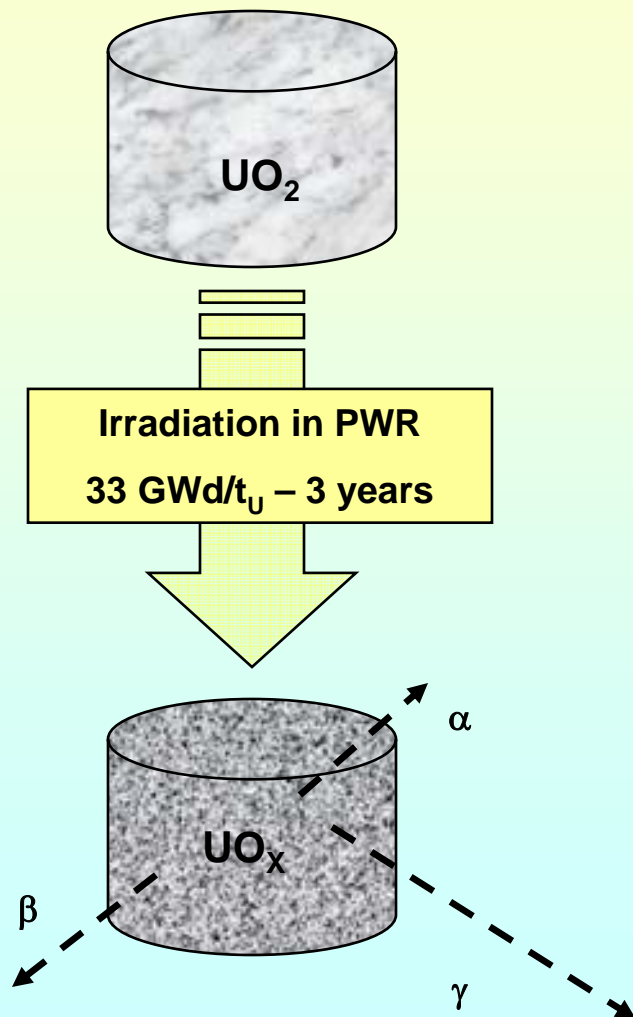


Review of Spent Fuel matrix Alteration with respect to Alpha-Radiolysis

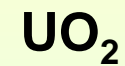
Jean Francois Lucchini

**Los Alamos National Laboratory,
Earth and Environmental Science Division,
EES-12, Carlsbad Operations
Actinide Chemistry and Repository Science Program
Carlsbad, NM USA
LA-UR-05-9617**

PWR Nuclear Fuel



Fresh Nuclear Fuel



3.5% ^{235}U enriched

Spent Nuclear Fuel

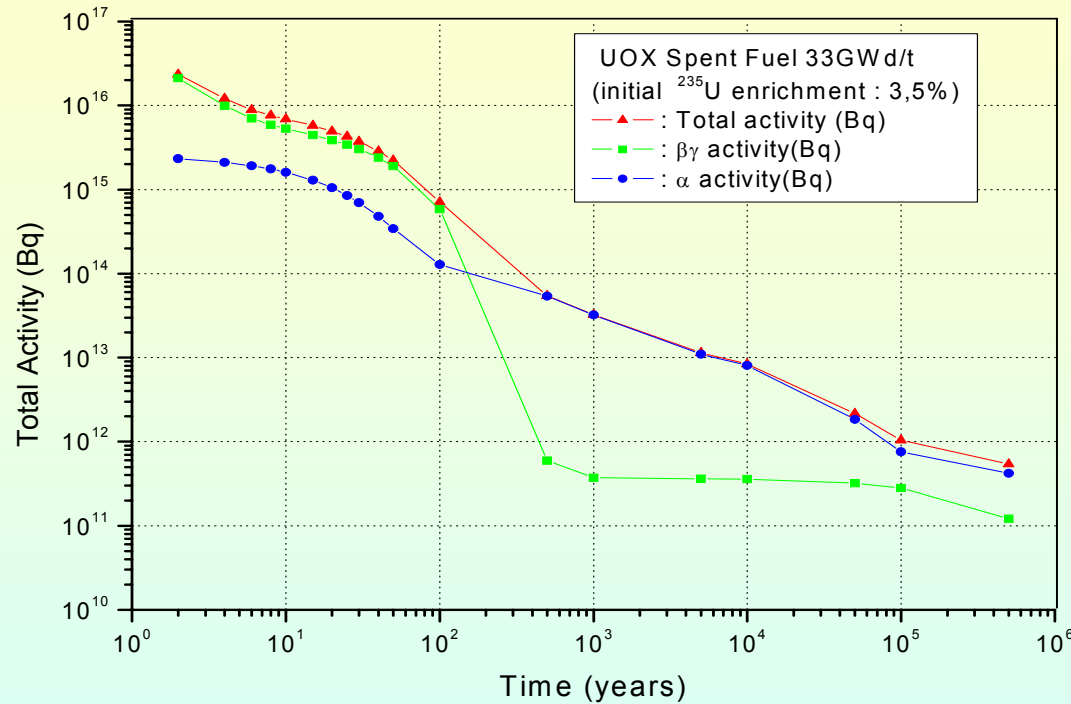
After 3 years of storage:

95 wt% UO_2

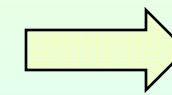
1 wt% transuranics (Pu, Np, Am, Cm)

4 wt% fission products (lanthanides, I, Sr, Cs, ...)

Long-term evolution of spent fuel ?

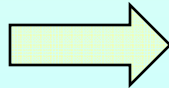


Lucchini J.F. (2001). "Effect of Water Alpha Radiolysis on the Spent Nuclear Fuel UO_2 Matrix." Thesis, University of Paris XI Orsay, France.

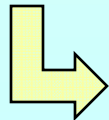


α activity
dominates on the
long-term

❖ On the long-term : possible contact between UO_x and water



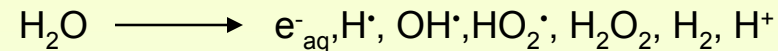
Release of radionuclides in the environment



Study of radiolysis effect on spent nuclear fuel alteration

Water radiolysis

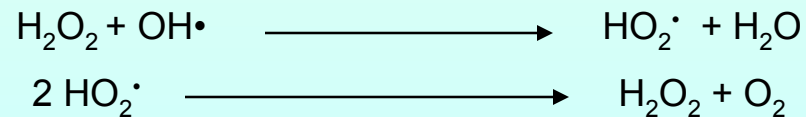
- ❖ In the course of water radiolysis, the following radical, ionic and molecular species are generated:



- ❖ Radiation-chemical yields.

LET (keV.μm ⁻¹)	radiation	g-values (number of species formed per 100eV energy absorbed)						
		e ⁻ _{aq}	H [•]	OH [•]	HO ₂ [•]	H ₂ O ₂	H ₂	-H ₂ O
108	5 MeV α	0.42	0.27	0.54	0.07	1.08	1.11	2.84

- ❖ O₂ is not a direct radiolysis product. It comes from the decomposition of H₂O₂.



- ❖ The molecular products of water radiolysis are H₂, O₂, and H₂O₂.

The transient water radiolytic species can affect ...

❖ the acid-base equilibrium of the solution, as well as...

Acid – base equilibrium between water radiolysis products at 25°C

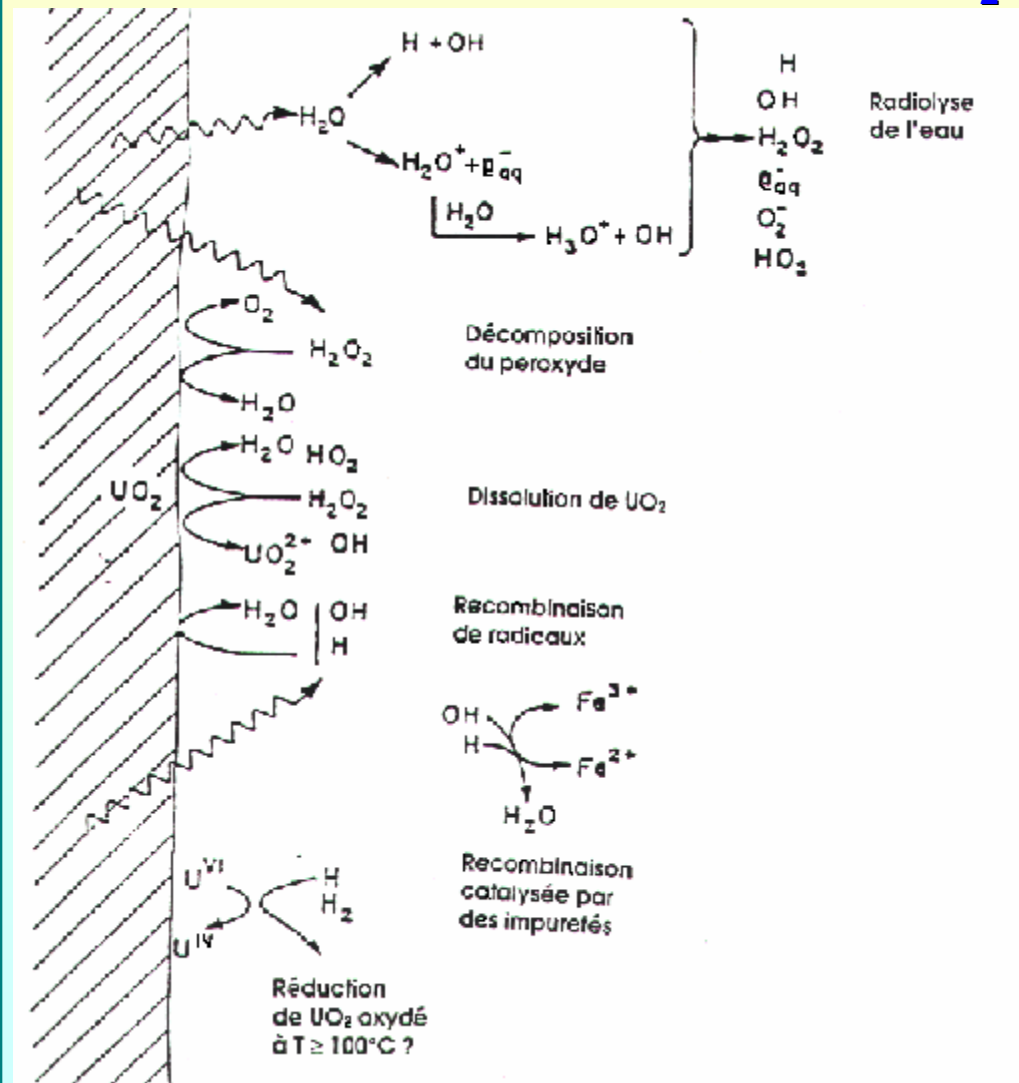
Couple	Reaction	pK_a
HO_2^* / O_2^-	$HO_2^* \leftrightarrow O_2^- + H^+$	4.8
H^* / e_{aq}^-	$H^* \leftrightarrow H^+ + e_{aq}^-$	9.6
OH^* / O^-	$OH^* \leftrightarrow H^+ + O^-$	11.9
H_2O_2 / HO_2^-	$H_2O_2 \leftrightarrow H^+ + HO_2^-$	11.9
H_2O / OH^-	$H_2O \leftrightarrow H^+ + OH^-$	14

Couple	Reaction	Redox Potential (V)
e_{aq}^- / H_2	$e_{aq}^- + H^+ \leftrightarrow \frac{1}{2}H_2$	-2.9
H^* / H_2	$H^* + H^+ + e^- \leftrightarrow H_2$	-2.3
O_2 / O_2^-	$O_2 + e^- \leftrightarrow O_2^-$	-0.3
H^+ / H_2	$H^+ + e^- \leftrightarrow \frac{1}{2}H_2$	0.00
O_2 / H_2O	$O_2 + 4H^+ + 4e^- \leftrightarrow 2H_2O$	1.23
O_2 / H_2O_2	$O_2 + 2H^+ + 2e^- \leftrightarrow H_2O_2$	0.695
HO_2^* / H_2O	$HO_2^* + 3H^+ + 3e^- \leftrightarrow 2H_2O$	1.35
H_2O_2 / H_2O	$H_2O_2 + 2H^+ + 2e^- \leftrightarrow 2H_2O$	1.78
OH^* / H_2O	$OH^* + H^+ + e^- \leftrightarrow H_2O$	2.7

❖ the redox conditions

Normal redox potentials of water and water radiolysis products (in Volt)

Formation and interactions of radiolytic species at the interface UO_2/water



The mechanism of the nuclear spent fuel alteration is the oxidative dissolution of the UO_2 spent fuel matrix. In contact with water, the spent fuel matrix constitutes a dynamic redox system depending upon the generation of oxidants and reductants at the spent fuel / water interface by alpha, beta and gamma radiolysis.

S. Sunder, D.W. Shoesmith, N.H. Miller. (1997) « Oxidation and dissolution of nuclear fuel (UO_2) by the products of the alpha radiolysis of water ». *Journal of Nuclear Materials* 244:66

NO CLEAR EFFECT of water radiolysis on spent nuclear fuel alteration is reported in the literature...

Experimental studies on spent fuel alteration in water have been going on since the late 1970s, using a variety of experimental conditions and solution compositions. None of these studies could determine a clear effect of water radiolysis on spent nuclear fuel alteration.

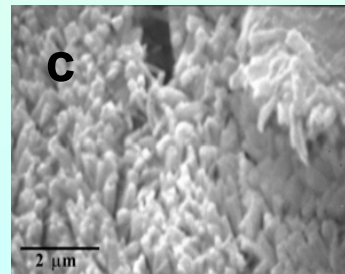
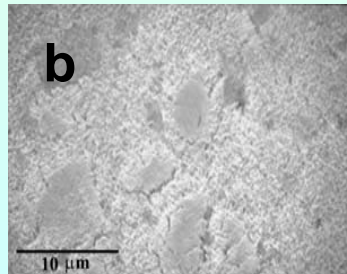
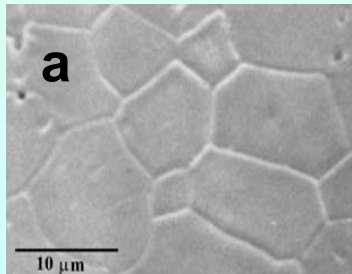
Nuclear spent fuel	Solution	Atmosphere	Time	Main results	Main conclusions	Team
PWR powder	10mM NaCl + 2mM NaHCO ₃	H ₂ +0.03% CO ₂ (0.5MPa)	More than one year	<ul style="list-style-type: none"> ☞ [U] ~ 10⁻⁹M ☞ Radiolytic O₂ levels below detection limit 	For [H ₂] _{dissolved} > 4mM, no measurable oxidative dissolution of UO ₂ matrix	SKB [Spahiu 2004]
PWR clad fuel rods of different burnup	Carbonated groundwater	Air	706 days	<ul style="list-style-type: none"> ☞ Constant Sr release factors : 2.7×10⁻⁸ d⁻¹ ☞ High Sr / U release ratios ☞ No burnup effect ☞ No measurable [H₂O₂] 	<ul style="list-style-type: none"> ☞ Alteration limited by the transport and accessibility of oxidizing species within the spent fuel segments ☞ Characterization of uranium secondary phases is needed 	CEA [Jegou 2004]

Spahiu K., Cui D., Lundstrom M. (2004). "The fate of radiolytic oxidants during spent fuel leaching in the presence of dissolved near field hydrogen." *Radiochimica Acta* **92**:625.

Jegou C., Peugeot S., Broudic V., Roudil D., Deschanel X., Bart J.M. (2004). "Identification of the mechanism limiting the alteration of clad spent fuel segments in aerated carbonated groundwater." *Journal of Nuclear Materials* **326**:144.

...whereas CLEAR EFFECTS are observed on UO_2 under α or γ irradiation

Material	Solution	Atmosphere	Time	Main results	Main conclusions	Team
UO_2 disks irradiated by $3.3 \times 10^{11} \alpha \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$	Deionized water	Air	5 × 1h	<ul style="list-style-type: none"> ☞ $[\text{U}] = 9 (\pm 1) \cdot 10^{-6} \text{M}$ ☞ $[\text{H}_2\text{O}_2] = 3.5 (\pm 0.3) \cdot 10^{-3} \text{M}$ 	Formation of uranium peroxide on the interface UO_2 / water under α irradiation	CEA [Lucchini 2001]
UO_2 pellets doped with α emitters (^{238}Pu and ^{239}Pu)	Deionized water	Ar	30 days	<ul style="list-style-type: none"> ☞ $[\text{U}] = 6.0 (\pm 0.1) \cdot 10^{-7} \text{M}$ at $3.2 \times 10^6 \alpha \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ ☞ $[\text{U}] = 4.2 (\pm 0.5) \cdot 10^{-8} \text{M}$ at $3.3 \times 10^5 \alpha \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ ☞ $[\text{U}] = 1.0 (\pm 0.1) \cdot 10^{-8} \text{M}$ at $3.3 \times 10^4 \alpha \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ 	Leaching experiments performed in deaerated media after preleaching the surface show that alpha radiolysis does affect the dissolution, which varies with the alpha flux at the UO_2 /water interface	CEA [a] Jegou 2005]
α -doped UO_2 pellets in external γ source (^{60}Co 260Ci)	Deionized water	Air or Ar + 4% H_2	14 days 16 days	<ul style="list-style-type: none"> ☞ $[\text{U}] = 7.5 \times 10^{-6} \text{M}$ in air ☞ $[\text{U}] = 3.9 \times 10^{-7} \text{M}$ in Ar 	<ul style="list-style-type: none"> ☞ Presence of studtite in aerated media ☞ Influence of the cover gaz on radiolytic effects 	CEA [b] Jegou 2005]



Scanning electron microscopy (SEM) images of (a) unleached UO_2 surface and, (b) and (c) leached UO_2 surface in water after 5×1h of α -beam irradiation, showing metastudtite [Lucchini 2001]

Lucchini J.F. (2001). "Effect of Water Alpha Radiolysis on the Spent Nuclear Fuel UO_2 Matrix." Thesis, University of Paris XI Orsay, France.

a) Jegou C., Muzeau B., Broudic V., Poulesquen A., Roudil D., Jorion F., Corbel C. (2005). "Effect of alpha irradiation on UO_2 surface reactivity in aqueous media." *Radiochimica Acta* 93:35.

b) Jegou C., Muzeau B., Broudic V., Peugeot S., Poulesquen A., Roudil D., Corbel C. (2005). "Effect of external gamma irradiation on dissolution of the spent UO_2 fuel matrix." *Journal of Nuclear Materials* 341:62.

A single recent work on spent nuclear fuel alteration show evidence of radiolytic effects

Nuclear spent fuel	Solution	Atmosphere Temperatures	Time	Main results	Main conclusions	Team
PWR powder (30 years old – crushed 20 years ago)	Deionized water – low volumes (less than 10mL), decreasing in time	Air 25°C, 60°C, 75°C and 90°C	752 days	<ul style="list-style-type: none"> ☞ At short hydration times, metashoepite ($\text{UO}_3 \cdot x\text{H}_2\text{O}$) ☞ Over 2 years, only studtite ($\text{UO}_4 \cdot 4\text{H}_2\text{O}$) and metastudtite ($\text{UO}_4 \cdot 2\text{H}_2\text{O}$) on the surface 	<ul style="list-style-type: none"> ☞ Combined leachates and solids data indicate that the dissolved uranium had precipitated ☞ The precipitate carried with it relevant radionuclides (Cs, Sr, Tc), as well as actinides (Np, Pu) 	PNNL [Hanson 2005, McNamara 2005]

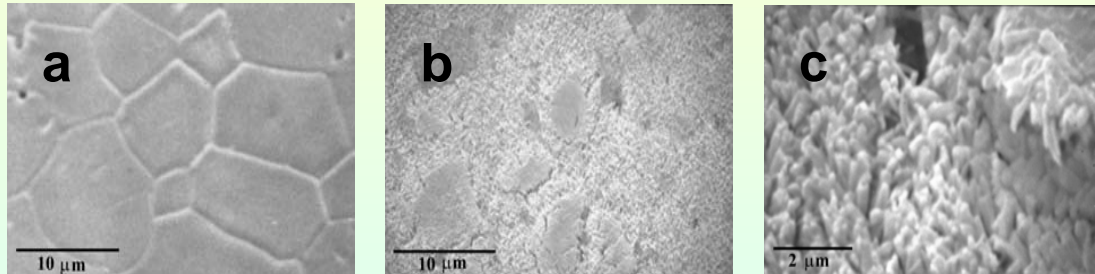
These data show a clear effect of water radiolysis on spent nuclear fuel corrosion under oxidizing conditions, at low material surface – water volume ratios and for long duration experiments. Formation of uranium peroxides is the consequence of a favorable rate of H_2O_2 production over the various scavenging processes.

Hanson B., McNamara B., Buck E., Friese J., Jenson E., Krupka K., Arey B. (2004). "Corrosion of commercial spent nuclear fuel. 1. Formation of studtite and metastudtite." *Radiochimica Acta* **93**:159.

McNamara B., Hanson B., Buck E., Soderquist C. (2005). "Corrosion of commercial spent nuclear fuel. 2. Radiochemical analyses of metastudtite and leachates." *Radiochimica Acta* **93**:169.

Uranium peroxides: formation, solubility and evidence in the environment

- ❖ When UO_2^{2+} is in the presence of hydrogen peroxide H_2O_2 , precipitation of uranyl peroxide occurs.
- ❖ The consequences of uranium peroxide precipitation are an increase of the specific surface of the material and an increase of its solubility. The solubilities of known uranium peroxides (studtite $\text{UO}_4 \cdot 4\text{H}_2\text{O}$ and metastudtite $\text{UO}_4 \cdot 2\text{H}_2\text{O}$) are about three orders of magnitude higher than the solubility of uranium dioxide UO_2 in the same conditions.



Scanning electron microscopy (SEM) images of (a) unleached UO_2 surface and, (b) and (c) leached UO_2 surface in water after $5 \times 1\text{h}$ of α -beam irradiation, showing metastudtite [Lucchini 2001]

- ❖ Studtite is the stable phase relative to dehydrated schoepite when H_2O_2 is present, but studtite is thermodynamically unstable in systems with no H_2O_2 . Even at initial H_2O_2 concentrations of 10^{-2}M , no UO_4 forms if there is a scavenger of H_2O_2 in solution [Amme 2002].
- ❖ However, if the peroxide concentration is high enough, the scavenging mechanism is overruled overtime and the formation of UO_4 takes place. This is the case of the natural formation of studtite minerals at the uranium deposits of Shinkolobwe in Shaba, Zaire and of Menzenschwand in the Black Forest, Germany. Studtite has also been identified as one of the uranium alteration phases in the Chernobyl lavas [Satonnay 2000].

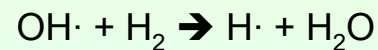
Lucchini J.F. (2001). "Effect of Water Alpha Radiolysis on the Spent Nuclear Fuel UO_2 Matrix." Thesis, University of Paris XI Orsay, France.

Amme M. (2002). "Contrary effects of the water radiolysis product H_2O_2 upon the dissolution of nuclear fuel in natural groundwater and deionized water." *Radiochimica Acta* **90**:399.

Satonnay G., Ardois C., Corbel C., Lucchini J.F., Barthe M.F., Garrido F., Gosset D. (2001). "Alpha radiolysis effects on UO_2 alteration in water." *Journal of Nuclear Materials* **288**:11.

Modeling: a good tool to predict radiolysis effect on nuclear spent fuel oxidation ?

- ❖ The simulation of experimental data was successfully used in order to predict UO_2 corrosion overtime under radiolysis [Christensen 1996].
- ❖ Varying parameters always help to reproduce experimental data.
- ❖ Modeling pointed out the key role of hydrogen consumption in the system, through the following reaction [Merino 2003] :



- ❖ However, it appears extremely difficult to simulate radiolysis effects on nuclear spent fuel, because of the extreme complexity of the material :
 - ✓ three different kinds of radiation (α , β , γ),
 - ✓ change of the dose rate overtime,
 - ✓ incomplete inventory of all the reactions involving radiolytic products and other elements from the spent fuel with correct kinetics constant values,...

Christensen H., Sunder S. (2002). " Evaluation of water layer thickness effective in the oxidation of UO_2 fuel due to radiolysis of water." Journal of Nuclear Materials **238**:70.

Merino J., Cera E., Bruno J. (2003). "Radiolytic Modelling: Application to Spent Fuel Dissolution Experiments." Material Research Society Symposium Proceedings **757**:421.

Conclusion

- ❖ Experimental studies performed so far, as well as modeling calculations, demonstrated that the radiolytic production of oxidants at the interface water/ UO_2 matrix should influence the oxidation/dissolution of spent nuclear fuel in an underground repository.
- ❖ However, significant progress needs to be addressed to determine quantitatively the impact of radiolysis on UO_2 corrosion overtime. Many processes can act as scavengers for radiolytic oxidants, and consequently can slow down or inhibit their effects:
 - ✓ reactions with reducing components in repository (e.g. Fe^{2+} , dissolved H_2),
 - ✓ formation of uranium secondary phases at the interface,
 - ✓ coprecipitation into uranium phases...
- ❖ In order to estimate the radiolysis effects on nuclear spent fuel alteration overtime in underground repository conditions, it is critical to determine the main processes that control the evolution in time of the oxidants/reductants balance at the interface, and the impact on the stability of UO_2 matrix and on the radionuclide release.