DE LA RECHERCHE À L'INDUSTRIE

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SPENT NUCLEAR FUEL CORROSION PROCESSES UNDER LONG TERM INTERIM STORAGE AND WASTE DISPOSAL CONDITIONS

C. Jégou, L. De Windt, V. Broudic, C. Martin, A. Ambard

OUTLINES

- Introduction
- Spent Fuel Corrosion processes under geological disposal
  - Radionuclides source terms
  - Spent fuel matrix alteration mechanisms : UOX fuel case
  - Spent fuel matrix alteration mechanisms : MOX fuel case
- Spent Fuel Corrosion processes under long term interim storage
- Conclusion

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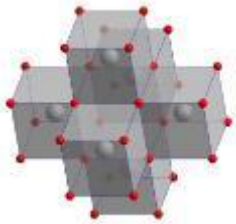
THE SPENT NUCLEAR FUEL

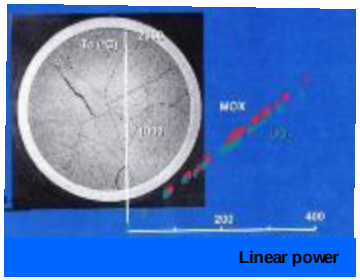


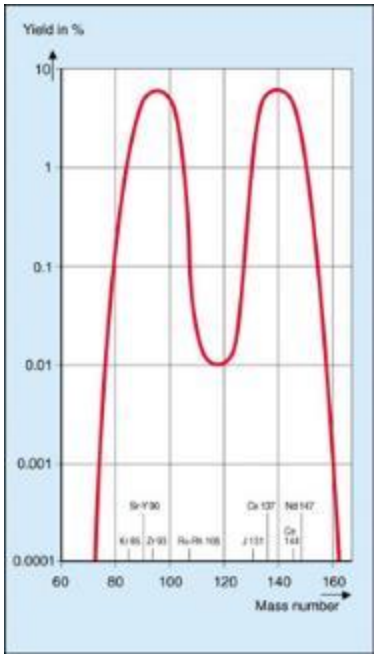
UO_2, PuO_2, $U_{1-y}Pu_yO_2$ …

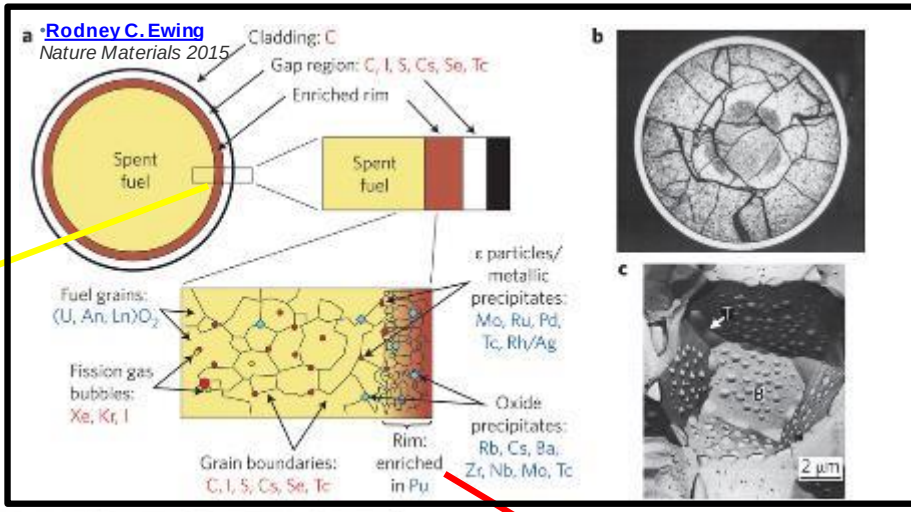
An initial Fluorite structure subjected to solicitations under irradiation

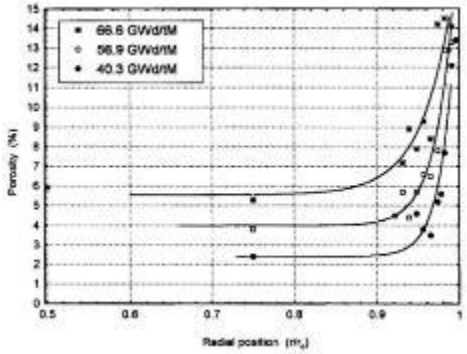
- Generation of fission products
- Radiation damage
- Thermal effects…

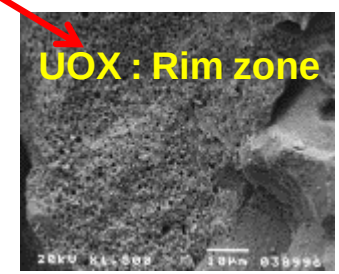
+ Microstructural evolutions





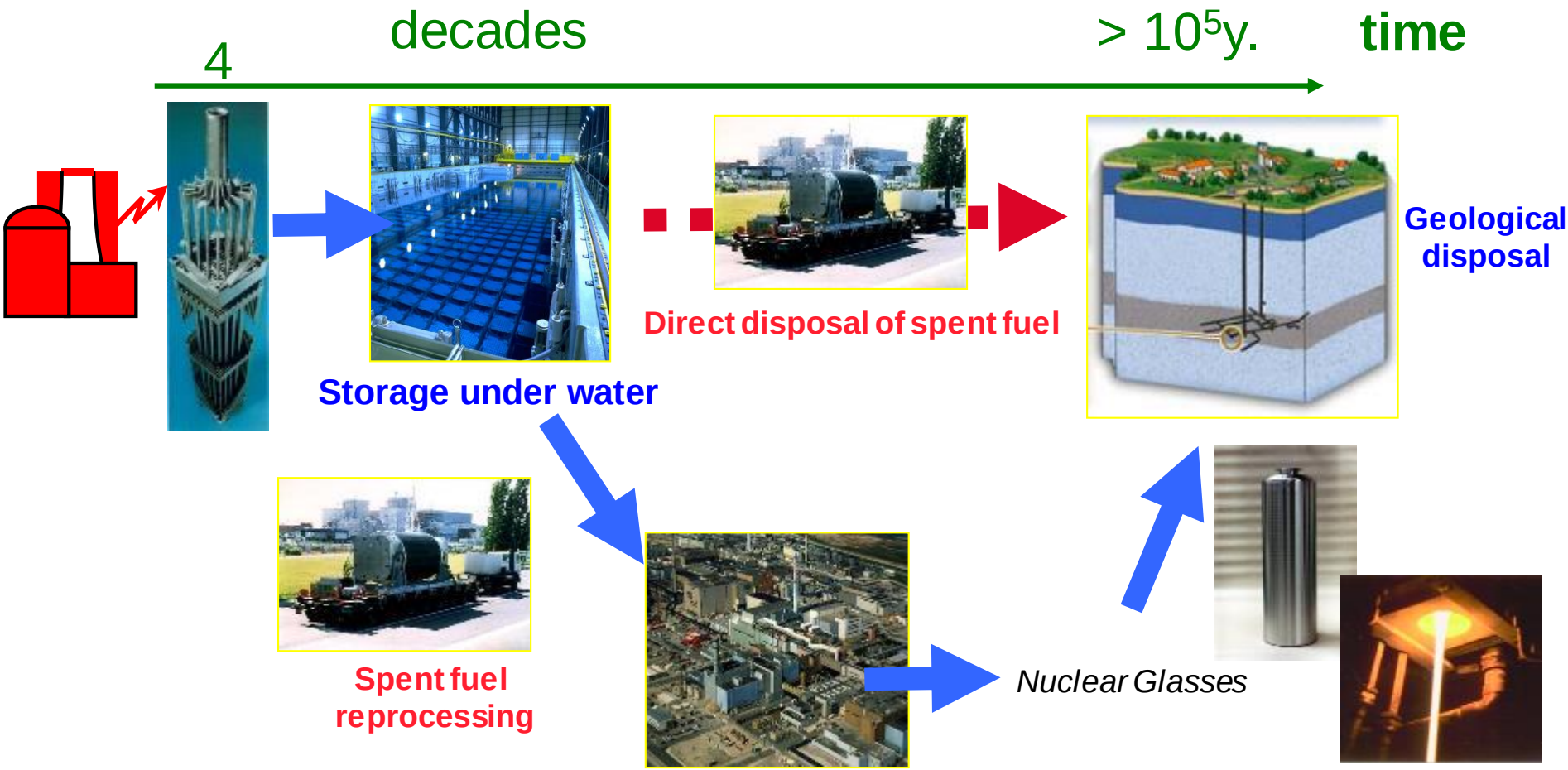






1. fission gases (fg) and other volatile elements: Br, Kr, Rb, I, Xe, Cs, Te;
2. fp forming metallic precipitates: Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Se, Te;
3. fp forming oxide precipitates: Rb, Sr, Zr, Nb, Mo, Se, Te, Cs, Ba;
4. fp dissolved as oxidesin the fuel matrix: Rb, Sr, Y, Zr, Nb, La, Ce, Pr, Nd, Pm, Sm, Eu.

Spent fuel management options



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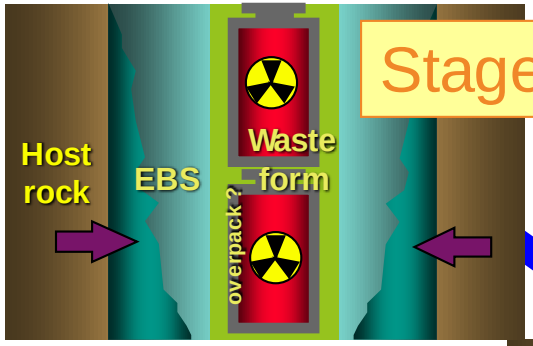
Expected evolution of SF in disposal

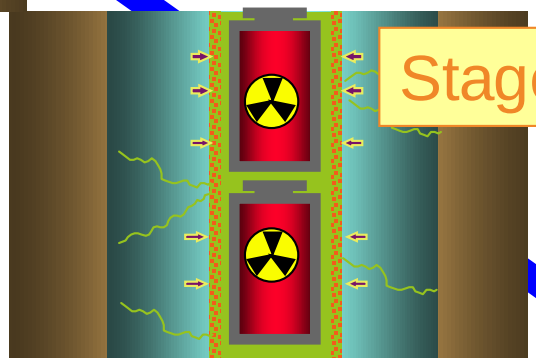


Stage I

Resaturation of the EBS

SF: intrinsic evolution

1 -- 1 ’000 y.



Stage II

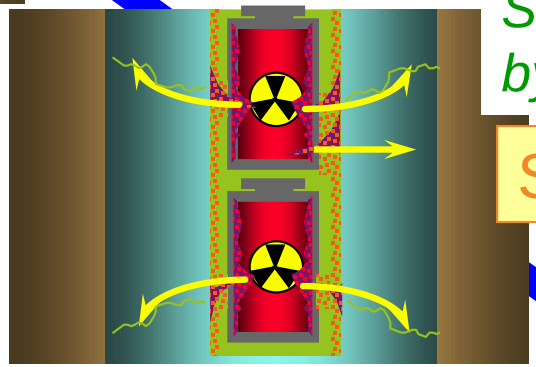
Corrosion of the container

SF: intrinsic evolution

500 -- 10 ’000 y.

Alteration of waste form

SF: alteration by water



Stage III

> 10 ’000 y.

Time

Intrinsic evolution of Spent Fuel in closed system prior to the access of water

Pellets — *Initially out-of-equilibrium => driving forces*

Thermal decrease → Evolution of the chemical state ($\Delta G(O_2)$...??)

Radioactive decay → Evolution of inventories → Evolution of the chemical state ($\Delta G(O_2)$...??)

Radioactive decay → Accumulation of irradiation defects → - Damages of the UO_2 matrix ? - RN migration ?

Radioactive decay → Helium production → Fate ?? µbubbles ? => swelling ? => release ?

Cladding
- Internal over-pressure (He (initial) + FG + He produced)
- damaged : hydrides, corrosion, irradiation damage

→ Breaching by long term creep strain

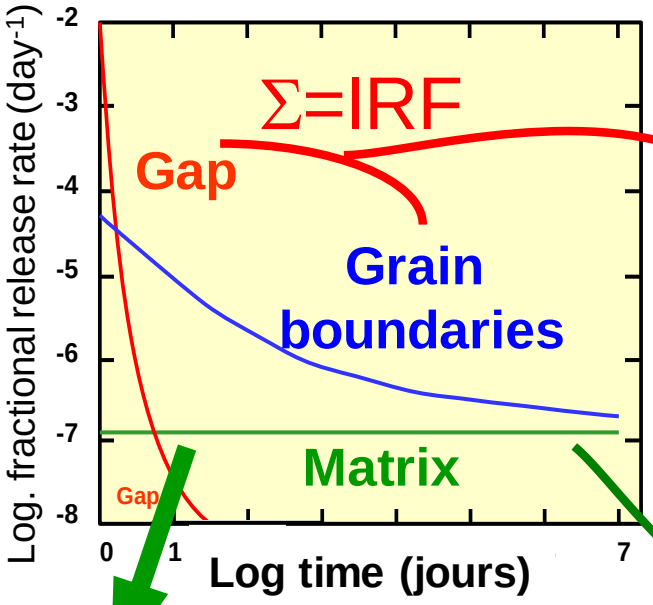
Effect of helium on the microstructure of spent fuel in a repository: An operational approach C. Ferry et coll. JNM 2010

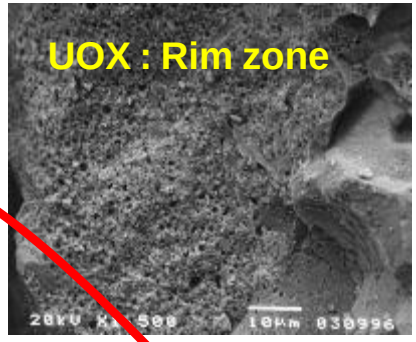
Impact of auto-irradiation on the thermophysical properties of oxide nuclear reactor fuels D. Staicu et coll. JNM 2010

Evolution of spent nuclear fuel in dry storage conditions for millennia and beyond T. Wiss et coll. JNM 2014

Spent fuel radionuclide source-term model for assessing spent fuel performance in geological disposal

Classical approach (Johnson et al.,1985)



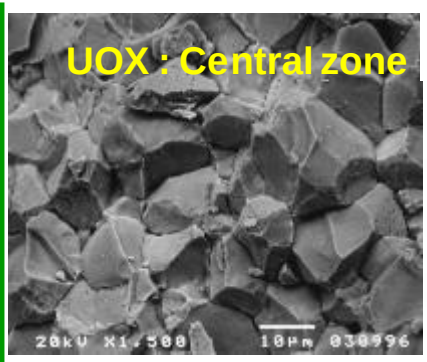


Fast release crucial for the long-term impact

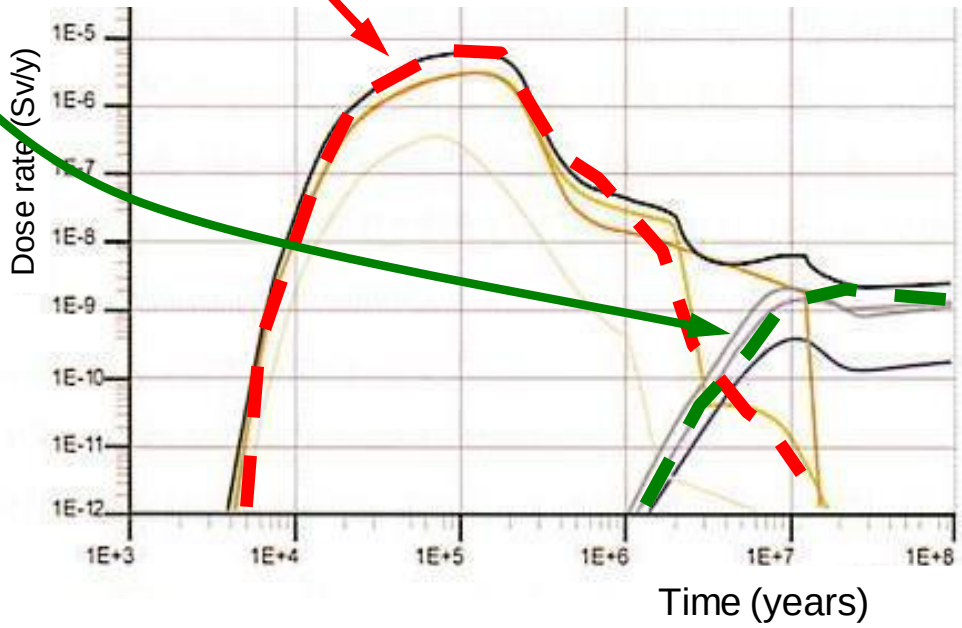
1

2

Matrix dissolution which drives the release of the radionuclides localized into the grains



SAFIR-2 Safety exercise (2001)



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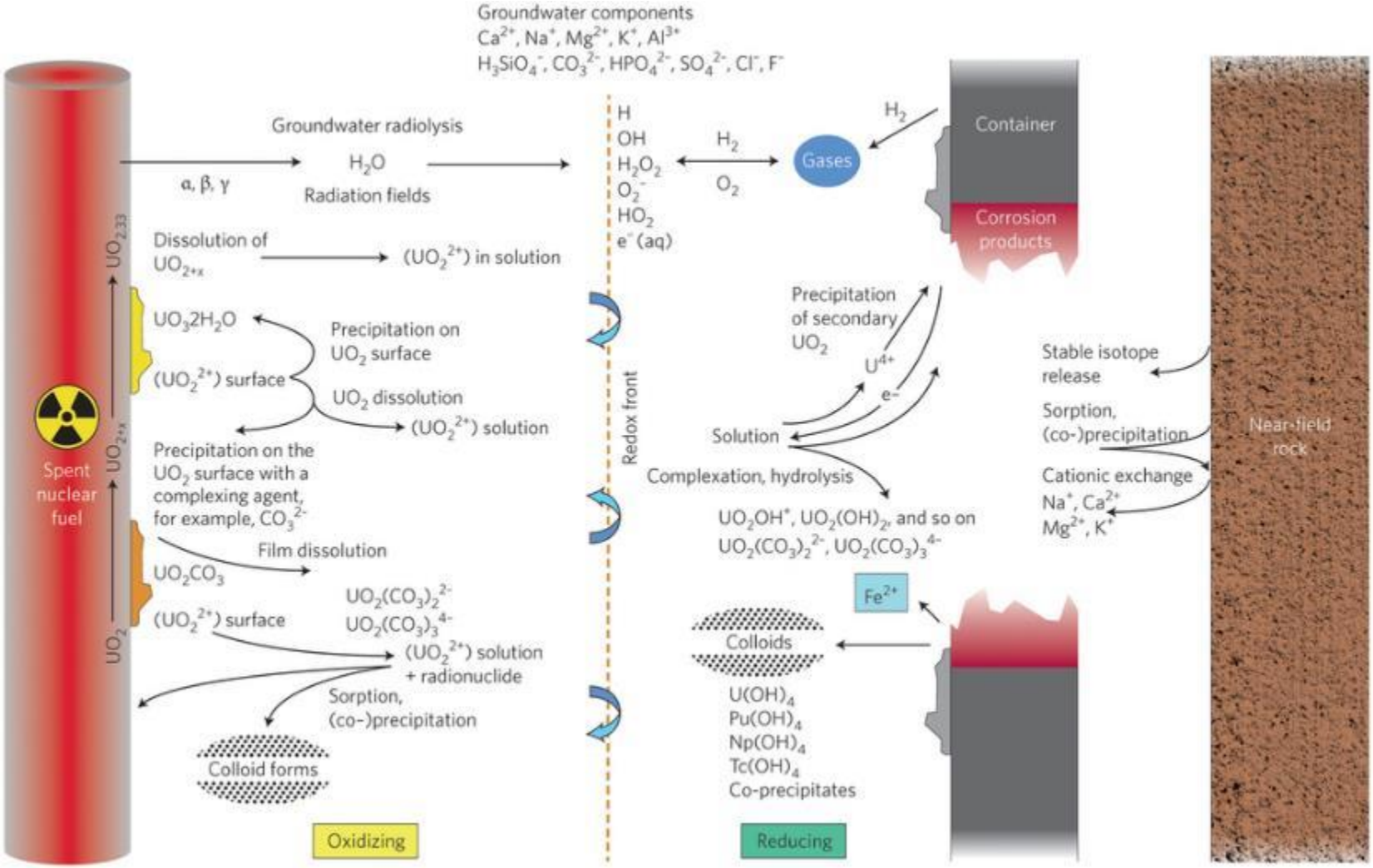
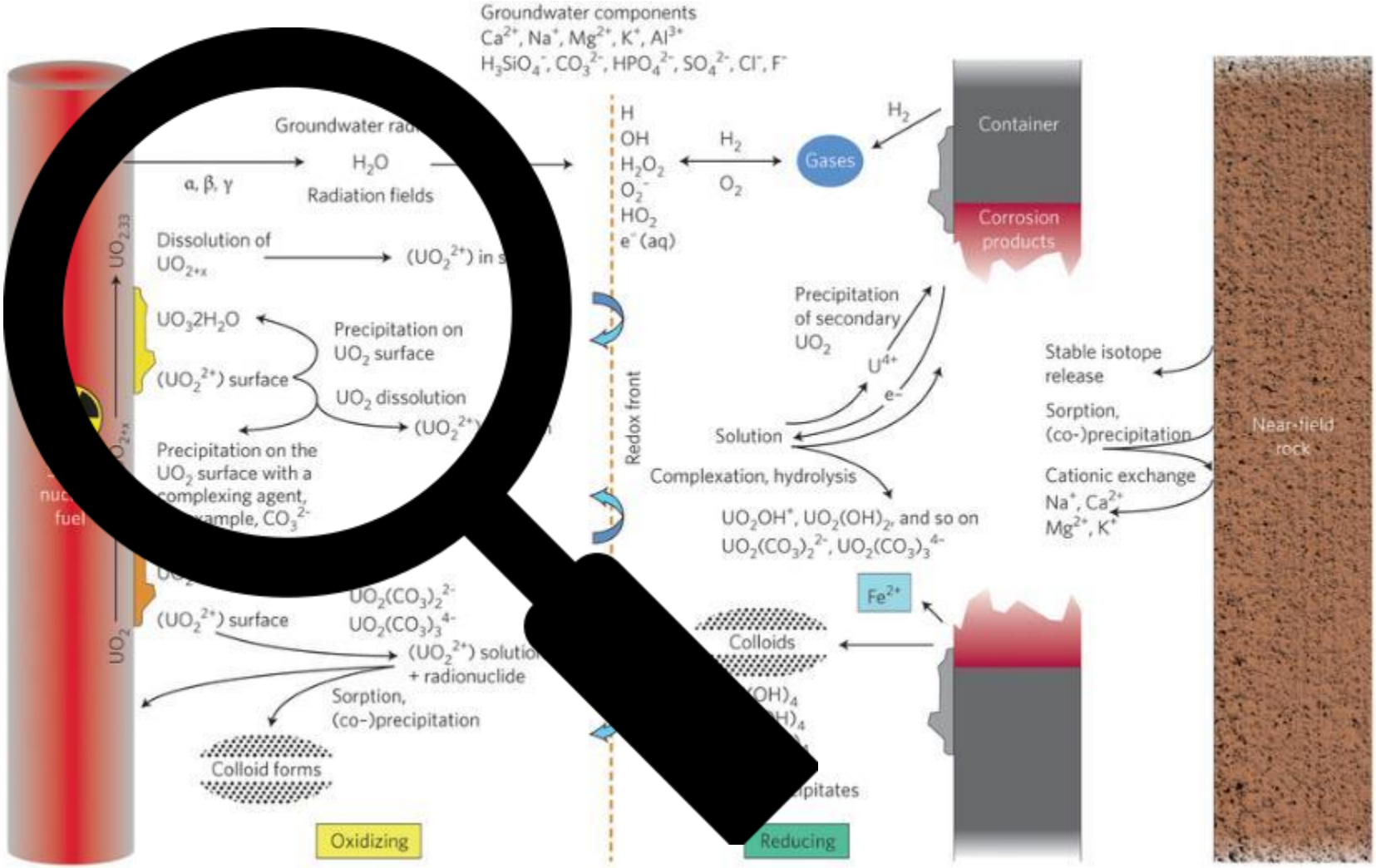
CHEMICAL PROCESSES THAT MAY AFFECT THE ALTERATION OF UOX SPENT FUEL IN CONTACT WITH GROUNDWATER



•**Rodney C. Ewing**
Nature Materials 2015

THE OXIDATIVE DISSOLUTION UNDER RADIOLYSIS



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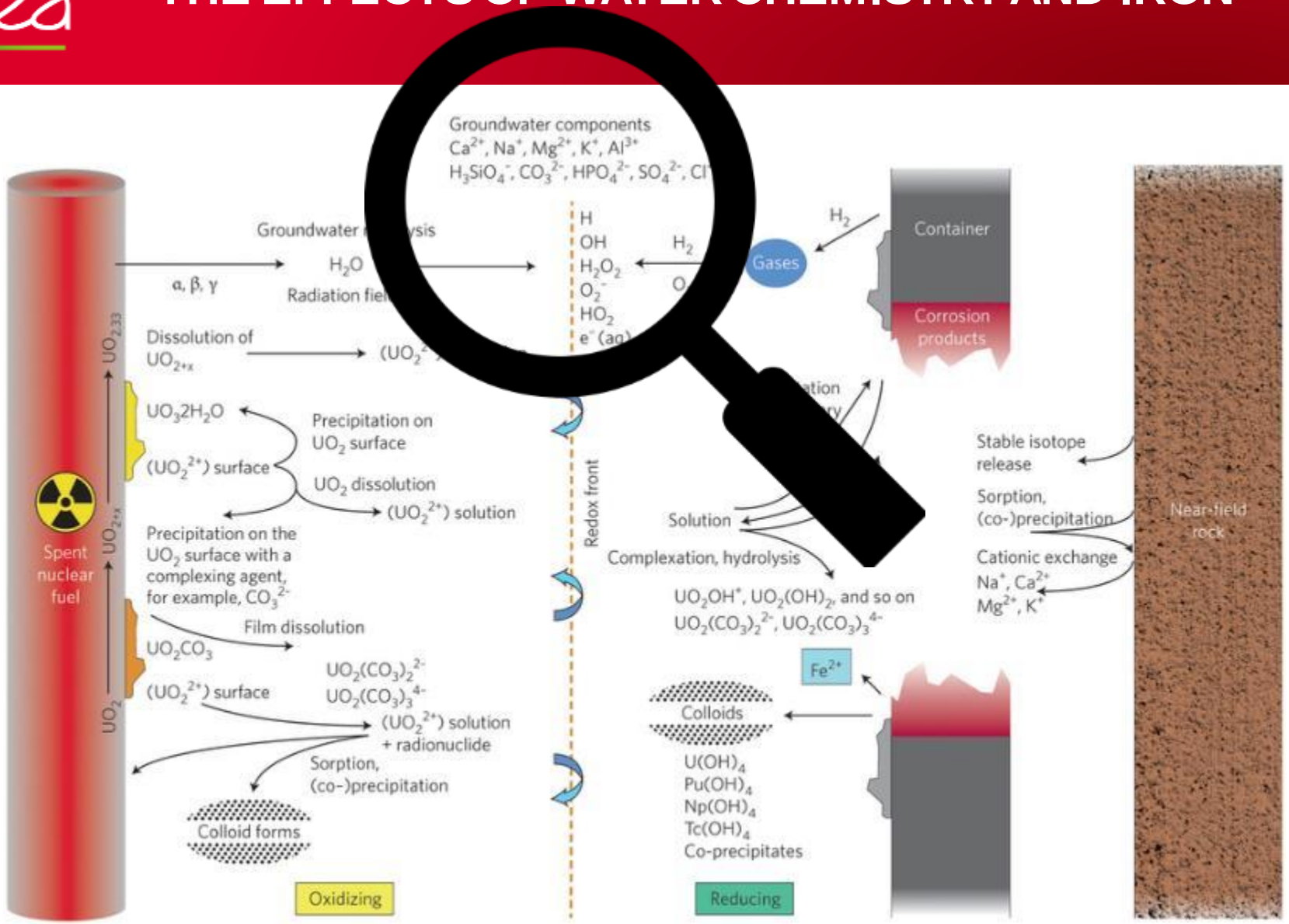
THE EFFECTS OF WATER CHEMISTRY AND IRON



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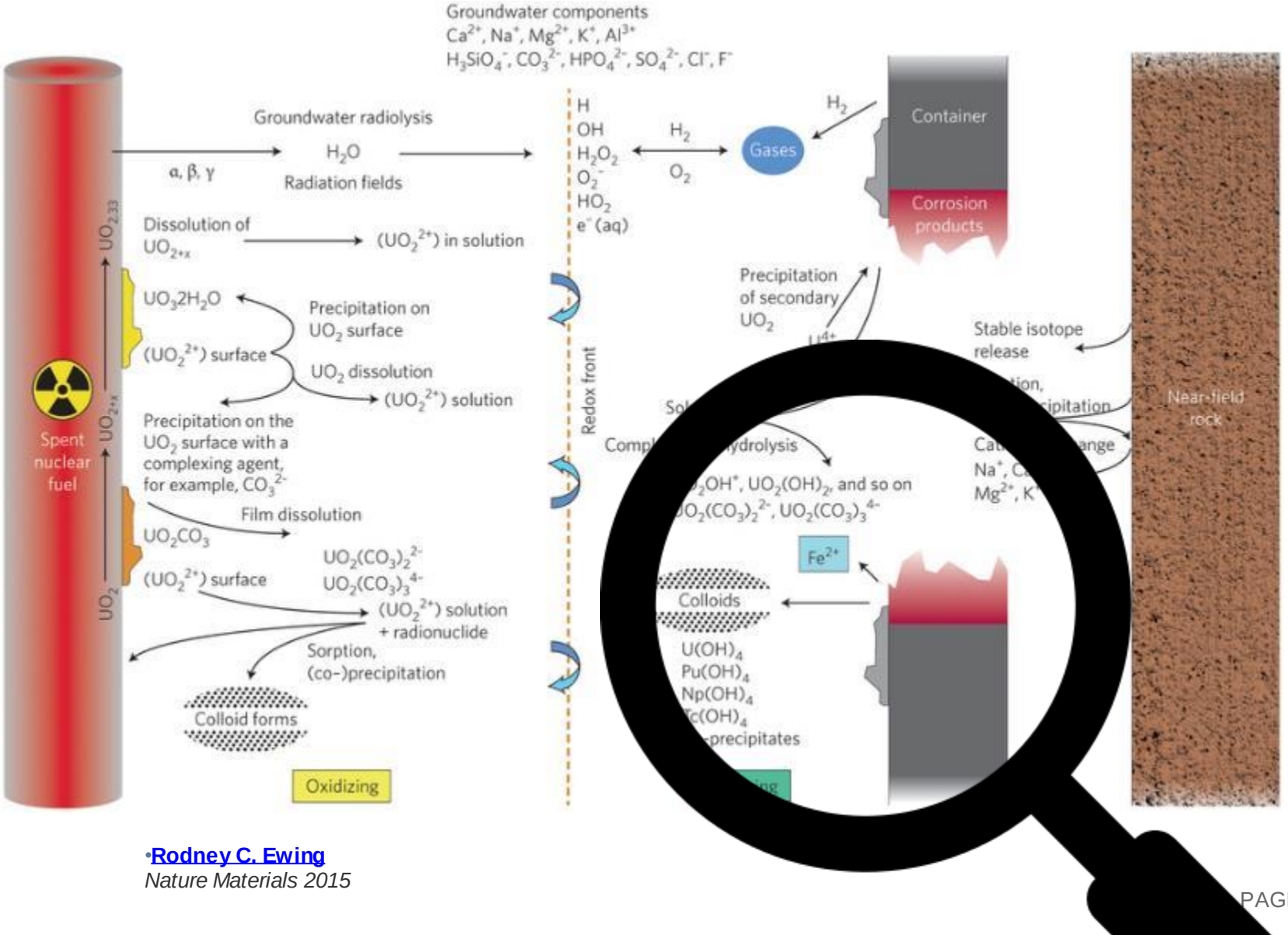

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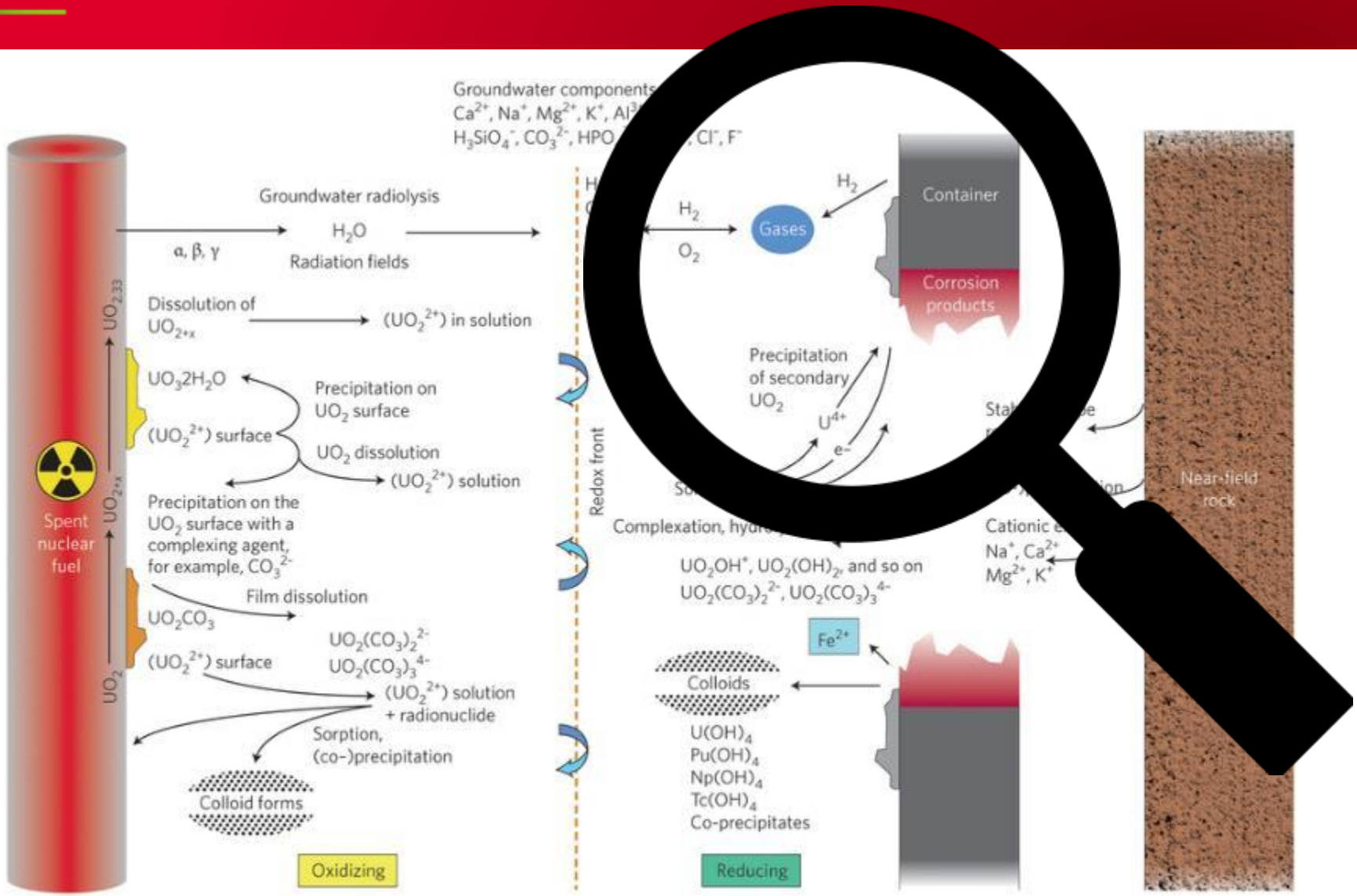
THE INHIBITORY EFFECT OF HYDROGEN



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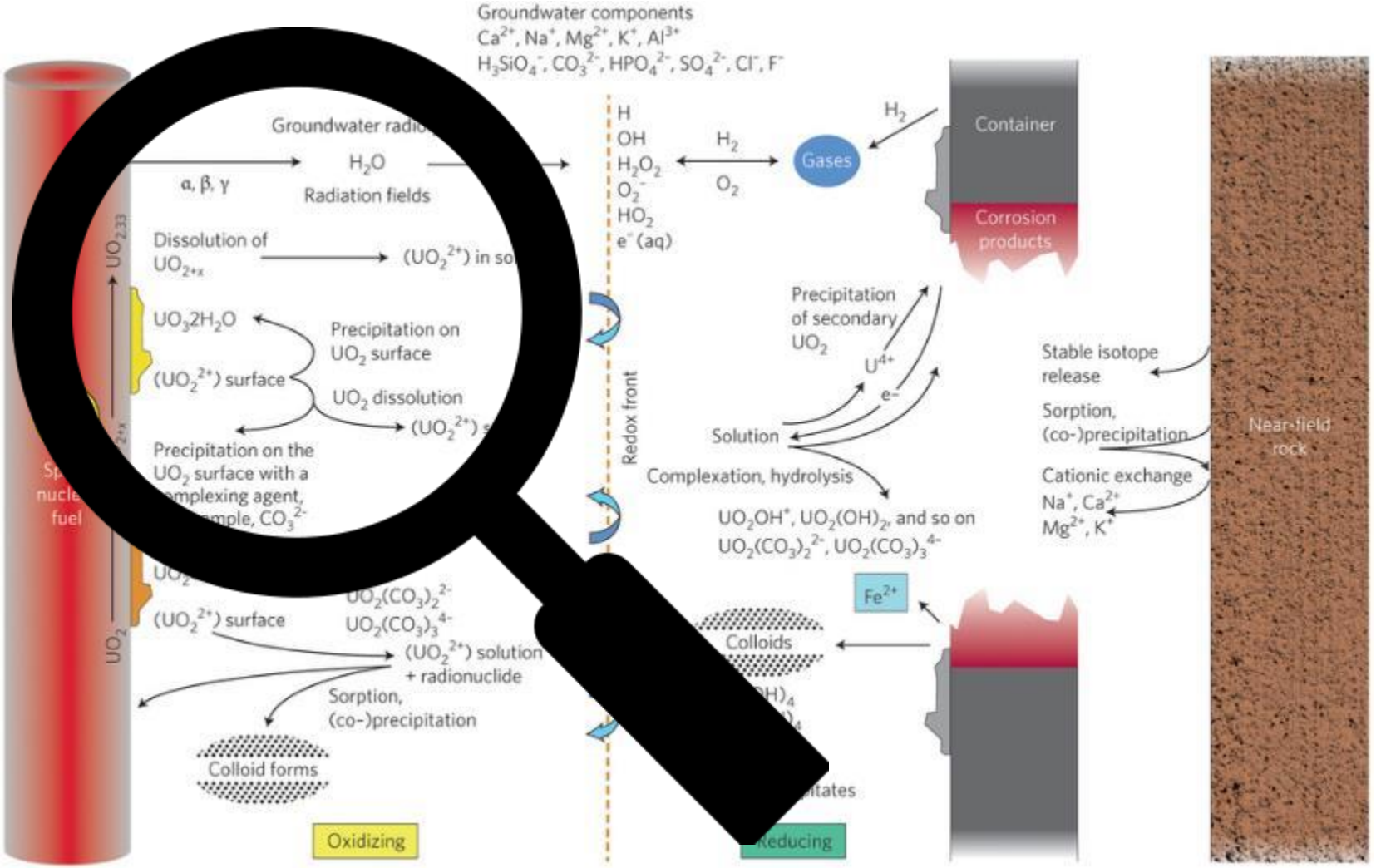

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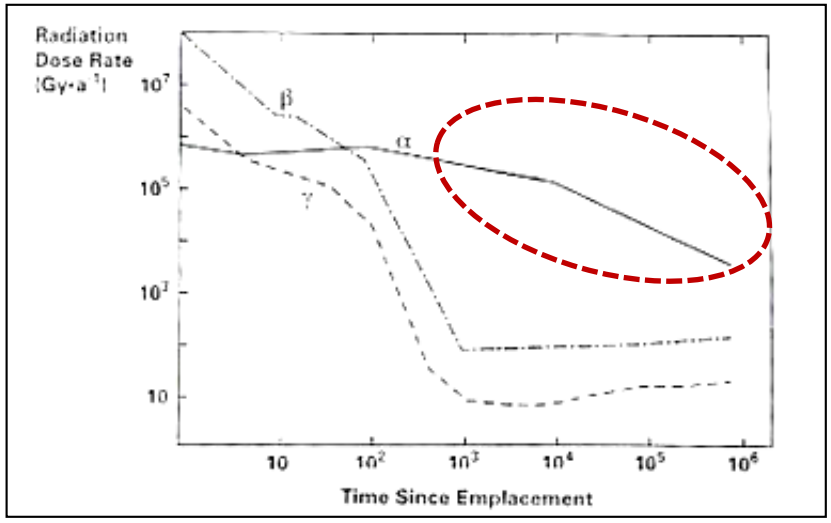
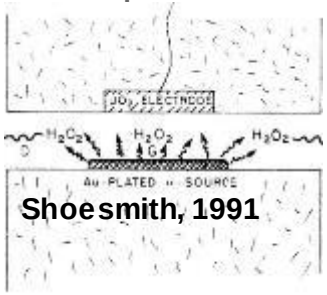
DOPED UO_2 PELLETS TO REPRESENT THE LONG TERM ACTIVITY OF SPENT FUEL

- 2 types of irradiation :
  - short term : βγ dominant
  - long term : α dominant → geological disposal

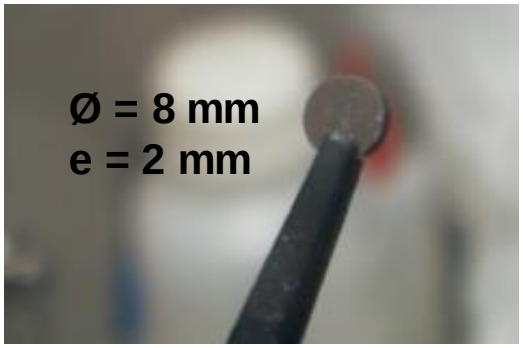


- 2 possibilities in laboratory :
  - External irradiation source
  - Pellets doped with α-emitters

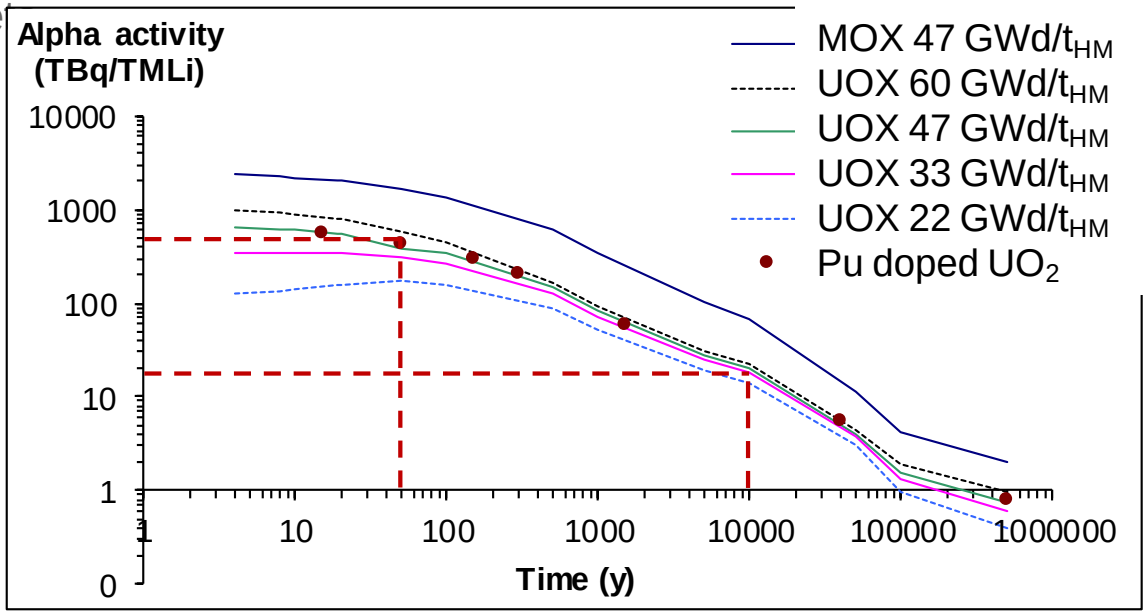


Shoesmith, 1991

- Pu-doped (or ^{233}U doped) UO_2 pellet
  - 15 to 40000 years UO_2
  - Reference UO_2



α-emitters doped UO_2 pellet

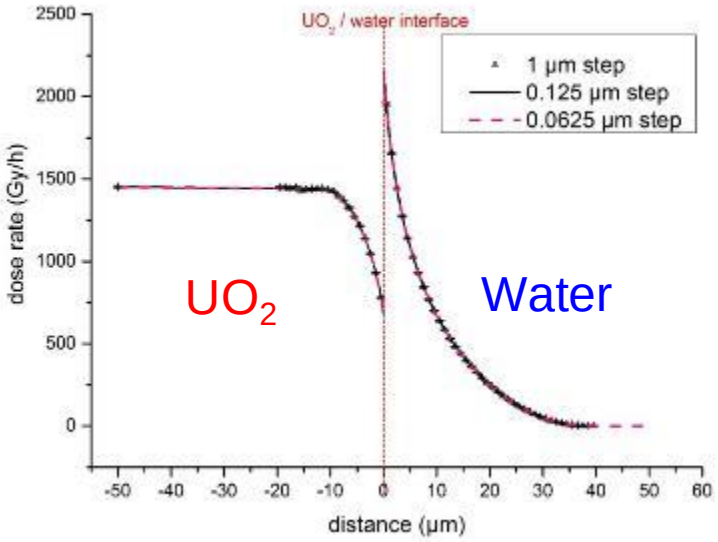


Alpha energy deposit profiles

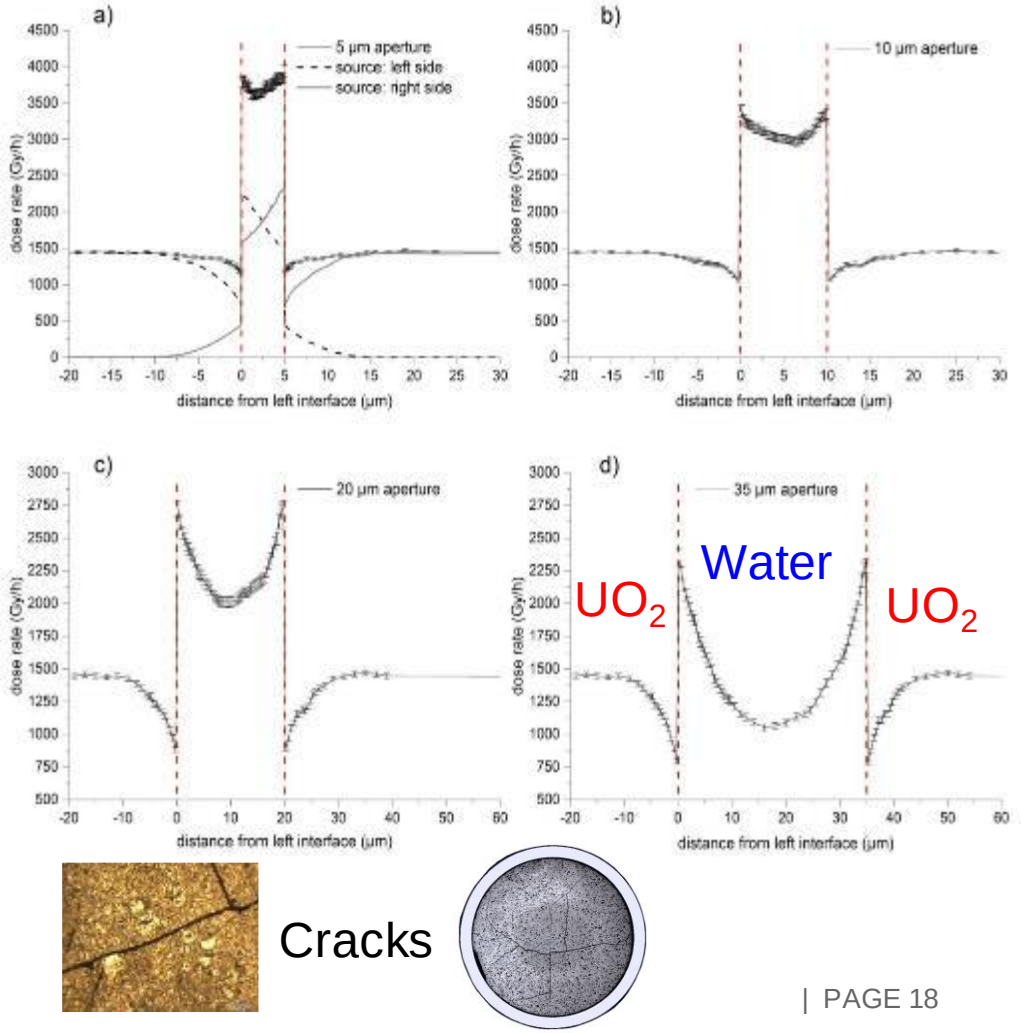
MCNPX® calculation code

alpha activity of 4.73×10^{8} Bq.g_{HM}^{-1} after 15 years of alpha decay (UOX47)

M Tribet et coll. 2016



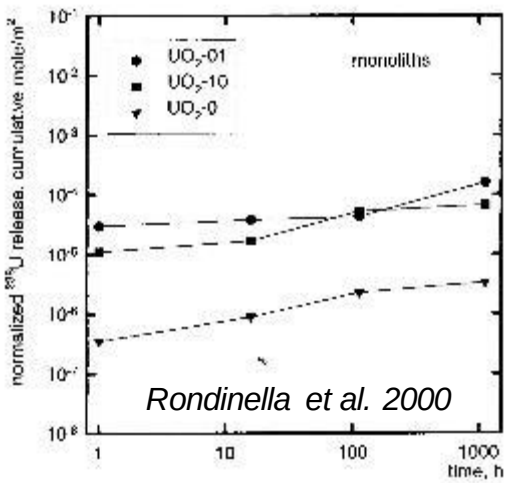
Flat surface



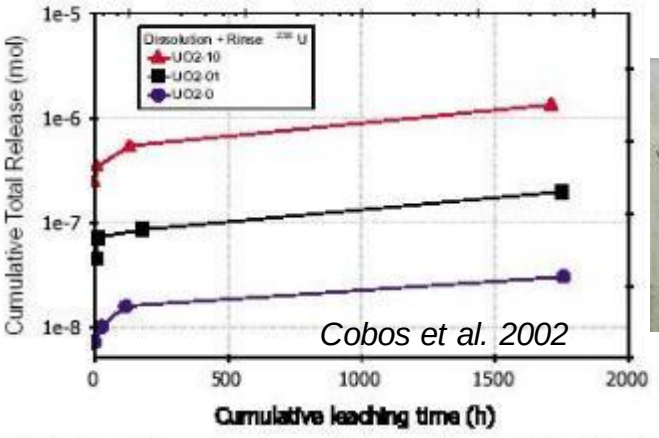
Cracks

Leaching of alpha doped UO_2 pellets **in pure water and anoxic media**

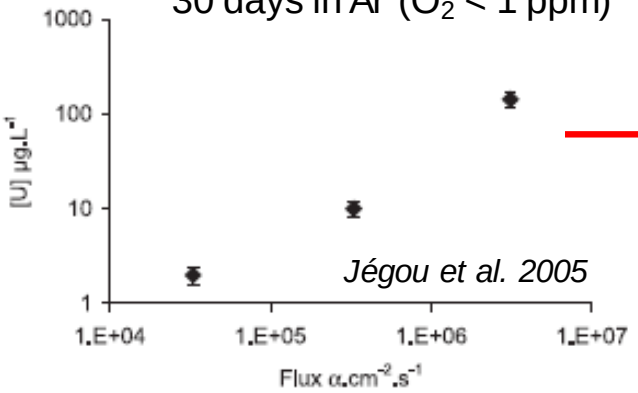
^{238}Pu doped UO_2 at 0, 0.1 et 10 %
Glove box N_2 (O_2 < 10 ppm)



^{238}Pu doped UO_2 at 0, 0.1 et 10 %
Glove box N_2 (O_2 < 0.4%)



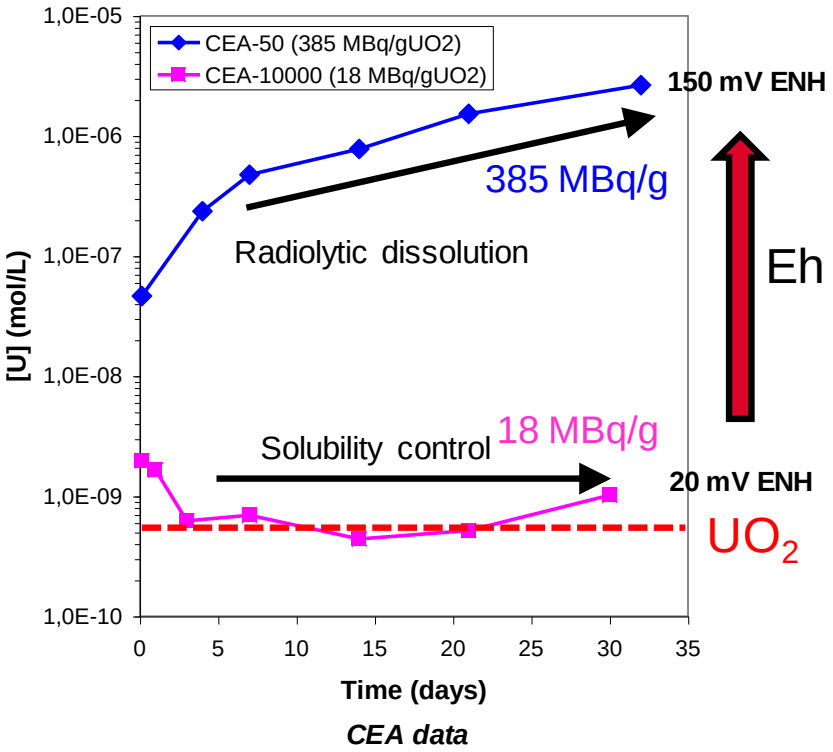
$^{238/239}Pu$ doped UO_2 at 0.2% Pu total
30 days in Ar (O_2 < 1 ppm)



Uranium release depends on the alpha activity of the UO_2 pellets

Specific alpha activity threshold in carbonated water

Uranium release under argon atmosphere in carbonated water ([$NaHCO_3$] = 1 mM)

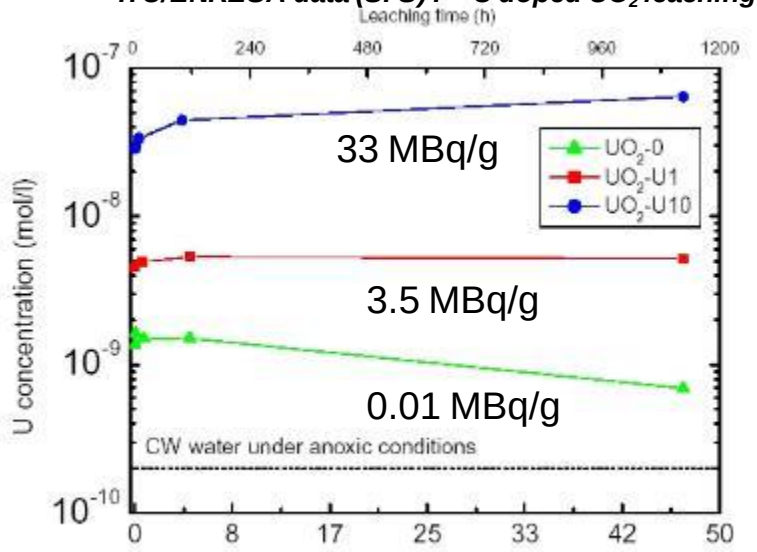


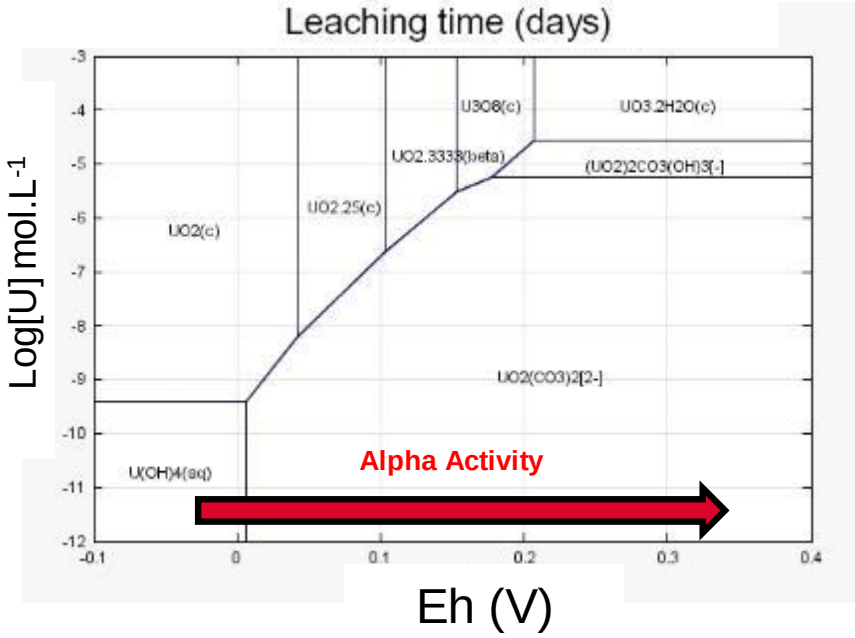
CEA data

Two release controls for uranium

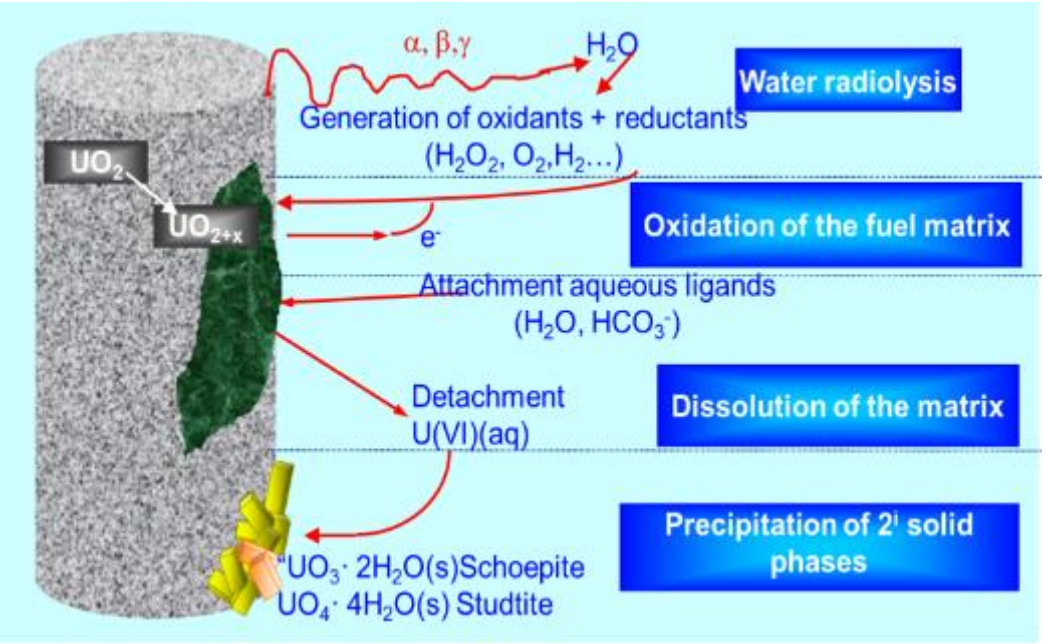
Definition of the specific activity threshold in anoxic carbonated conditions
→ between 18 and 33 MBq/g

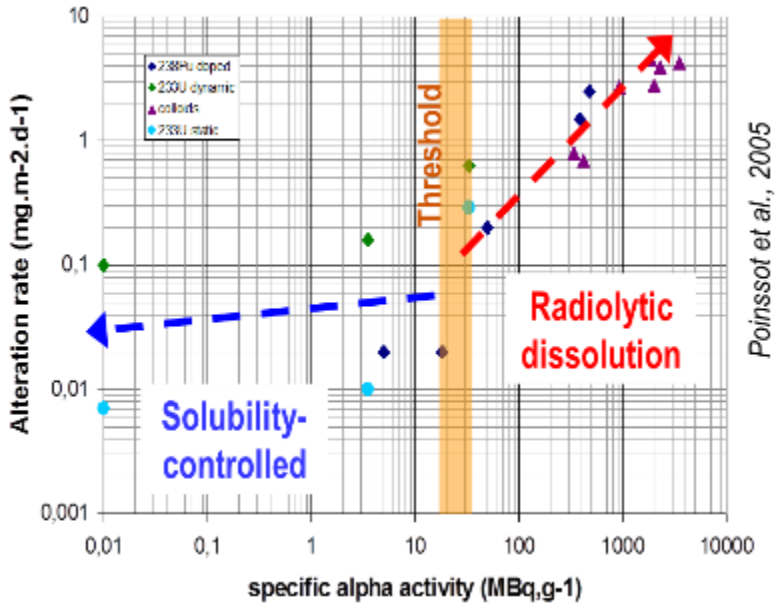
ITU/ENRESA data (SFS) : ^{233}U doped UO_2 leaching





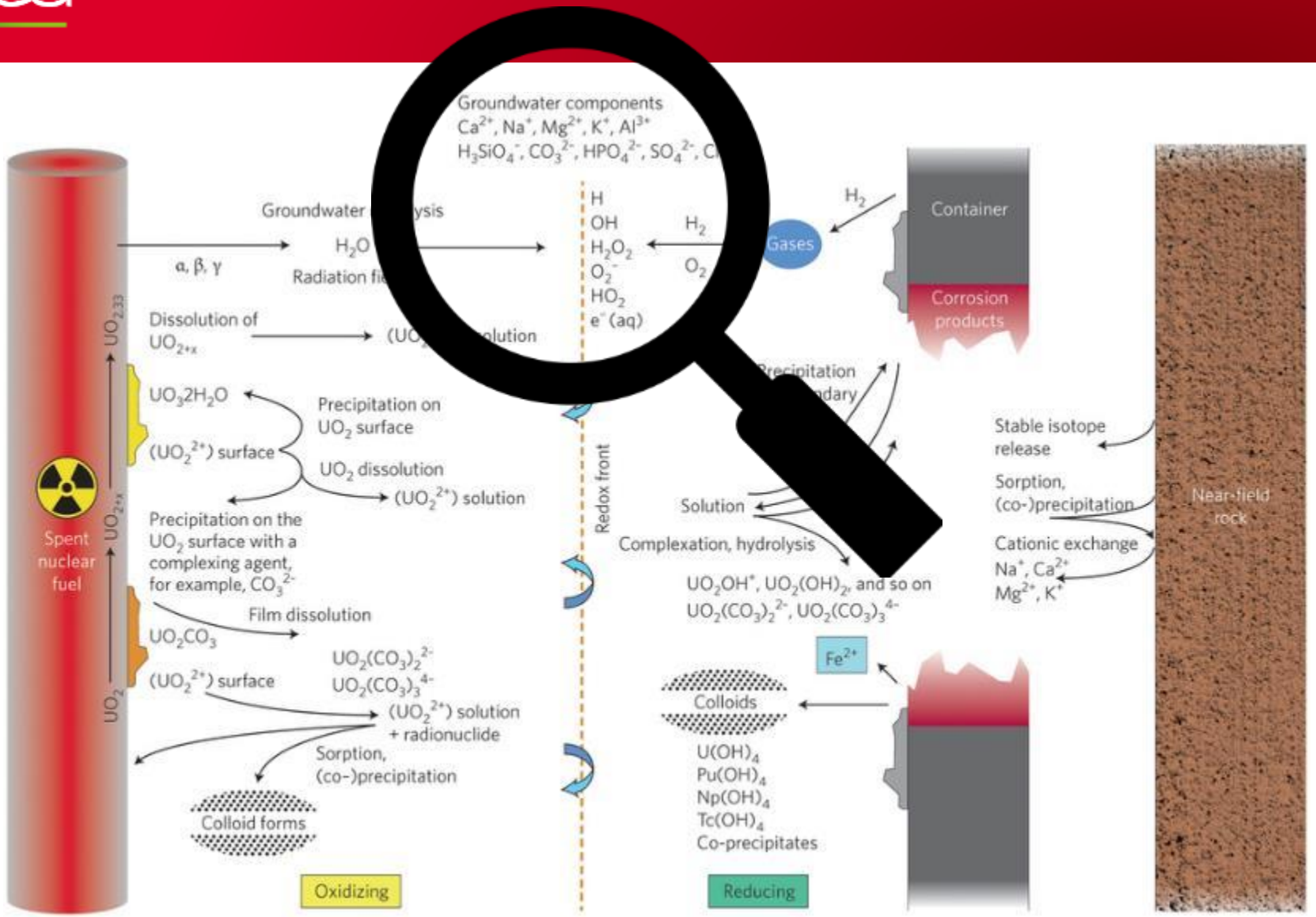
Specific alpha activity threshold **for simple systems**





European Project SFS - 2005

THE EFFECTS OF WATER CHEMISTRY AND IRON



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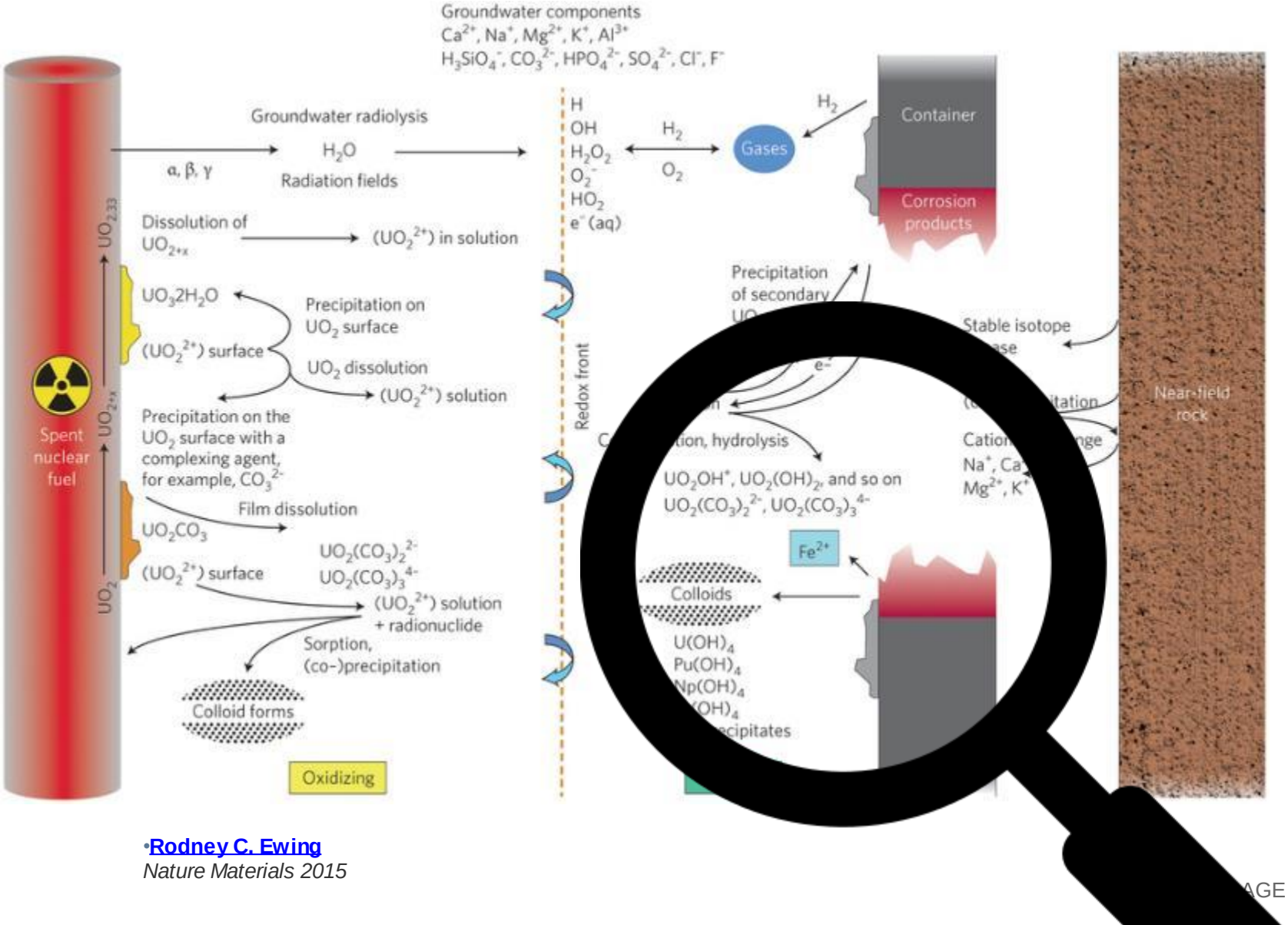

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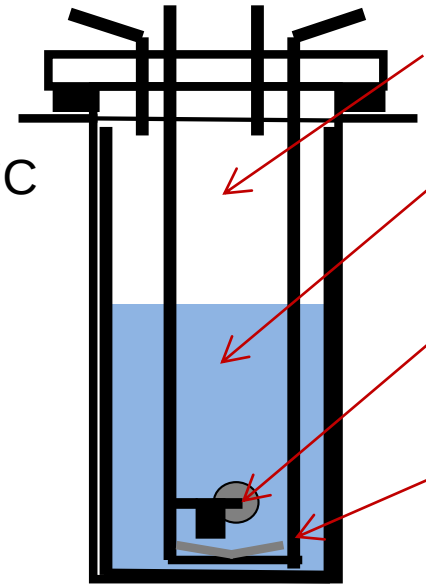
Influence of groundwater and metallic iron

T = 20 °C



Gaseous phase Ar/CO_2 3000 ppm (P = 3.5 bars)

↳ **anoxic conditions**

Synthetic ground water

↳ **Callovo-Oxfordian (COx) clay rock**

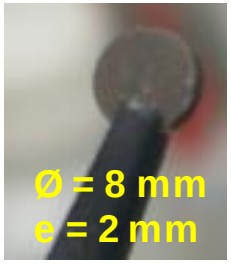
Pu-doped UO_2 pellets

↳ **alpha radiolysis of water**

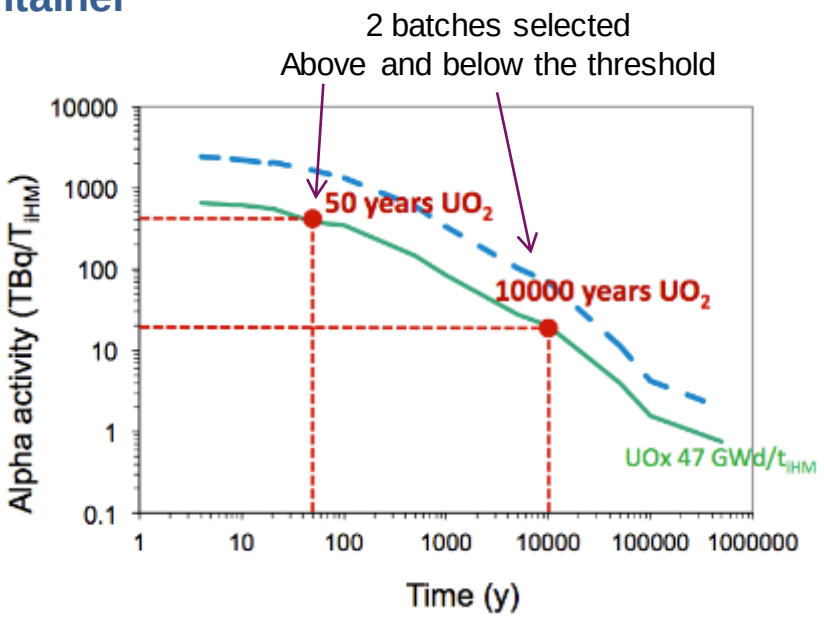
Metallic iron foil

↳ **steel container**

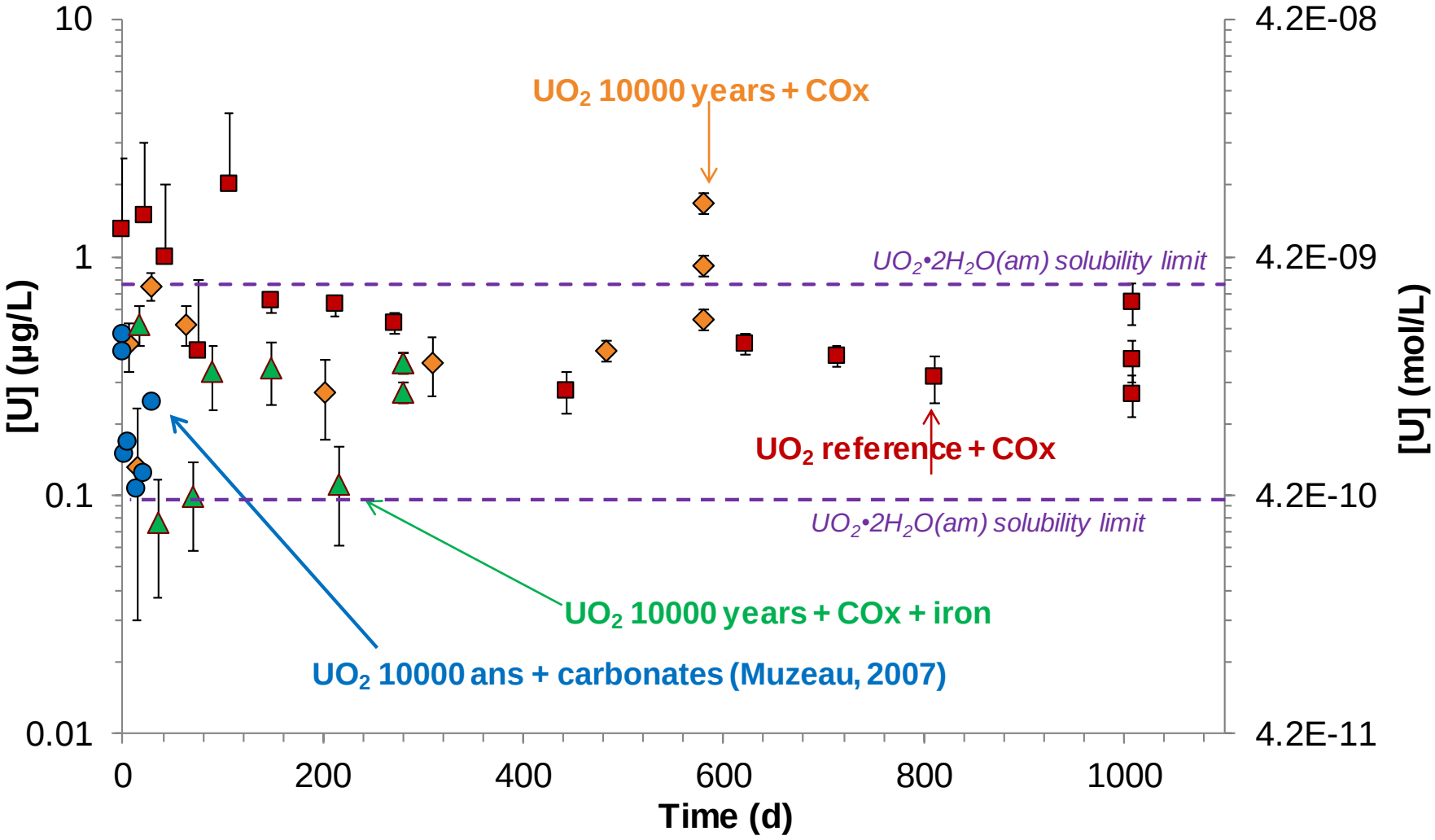
	pH	pe	Eh (mV)	PCO_2	Concentrations (mmol/L)										
					Al	Fe	Si	Sr	K	Mg	Ca	Na	Cl	S(6)	TIC	S(-2)
EST25687	7,1	-2,85	-168	-2,0	$4,7.10^{-5}$	0,034	0,18	0,20	1,03	6,67	7,36	45,6	41,0	15,6	3,34	$2,6.10^{-7}$
EST21400H	7,2	-2,90	-171	-2,0	$4,4.10^{-6}$	0,029	0,18	0,18	1,52	5,80	6,28	36,2	29,0	15,1	3,33	$2,7.10^{-7}$



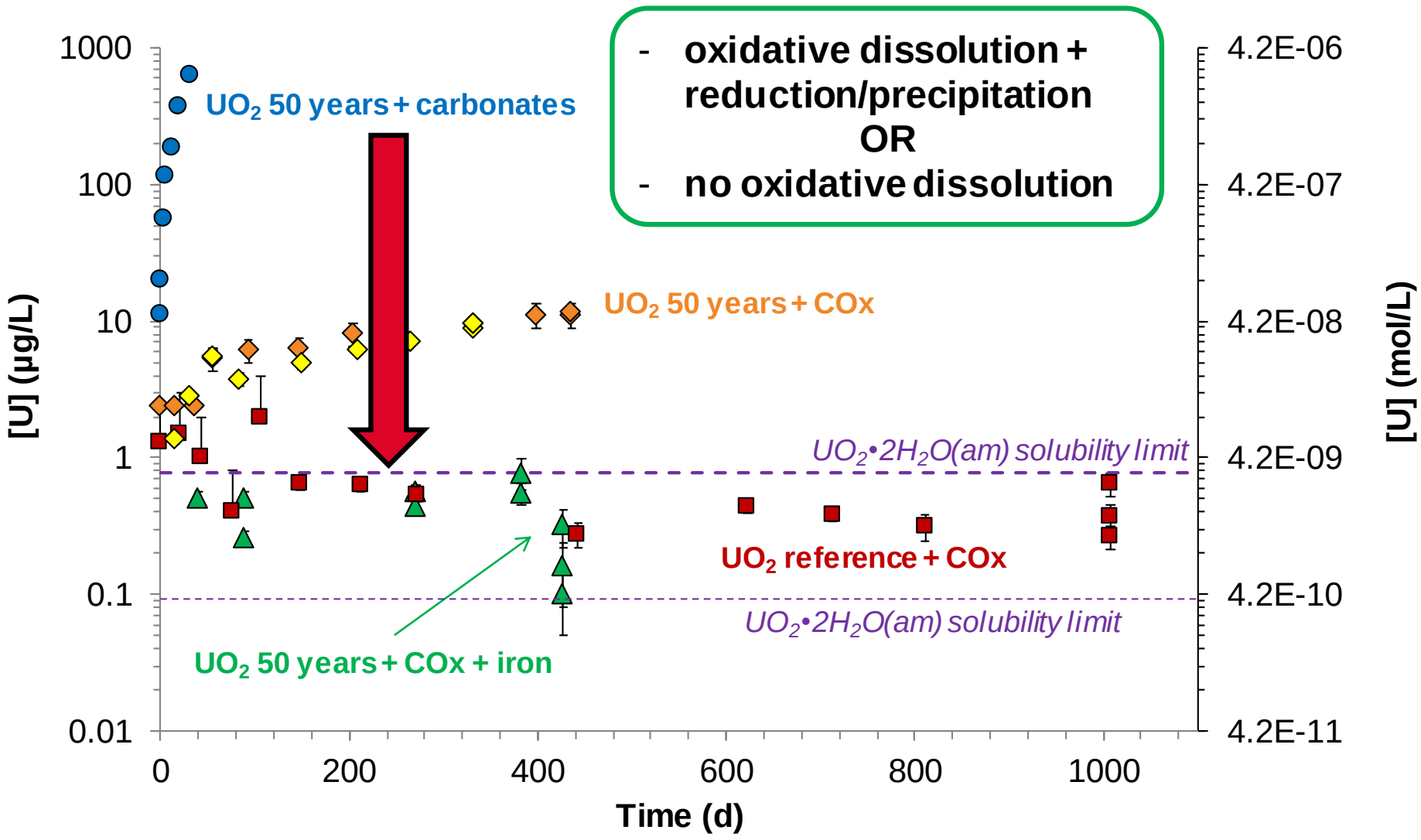
$(U_{0.997}Pu_{0.003})O_2$ grains



URANIUM CONCENTRATION: UO_2 10000 YEARS

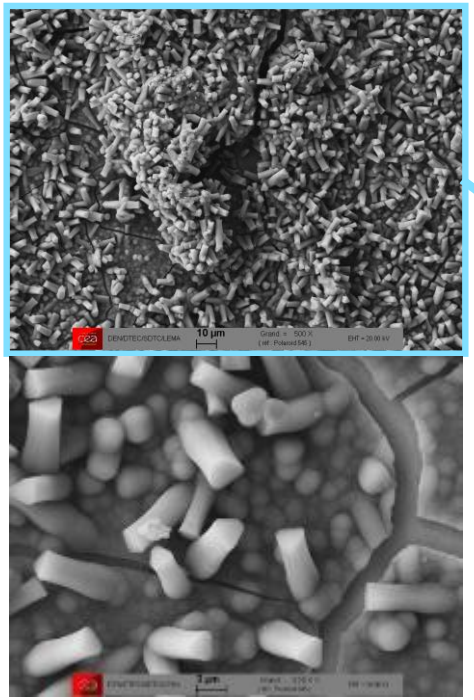


URANIUM CONCENTRATION: UO_2 50 YEARS



UO_2 PELLETS CHARACTERIZATIONS: SEM-EDS

SEM images: in collaboration with G. Jouan (CEA/LEMA)



Upper crust

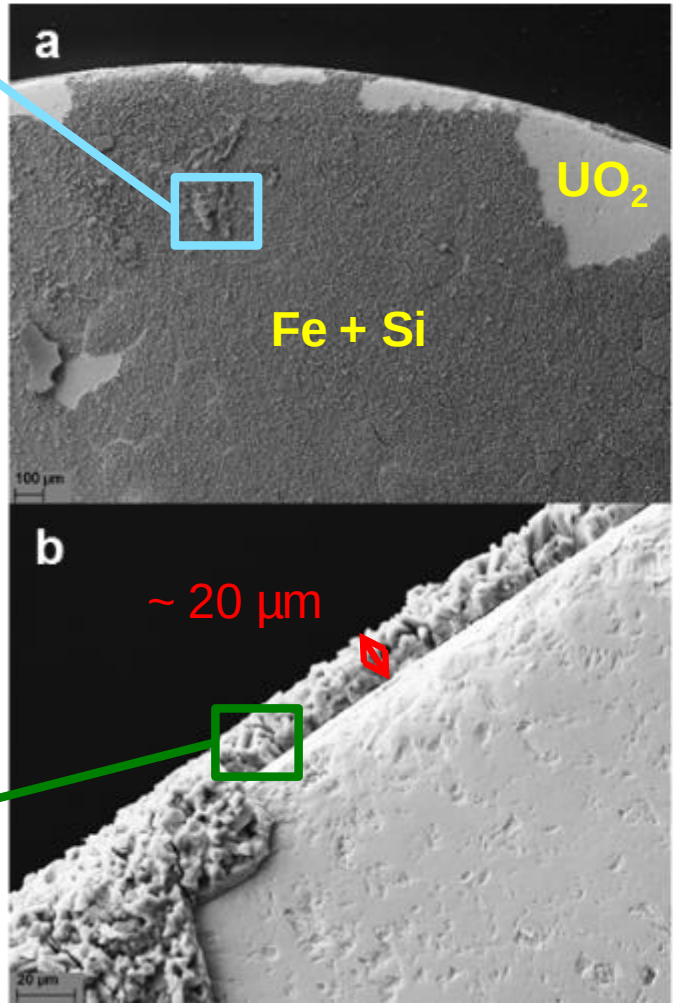
12 µm — 95% Fe, 5% Si

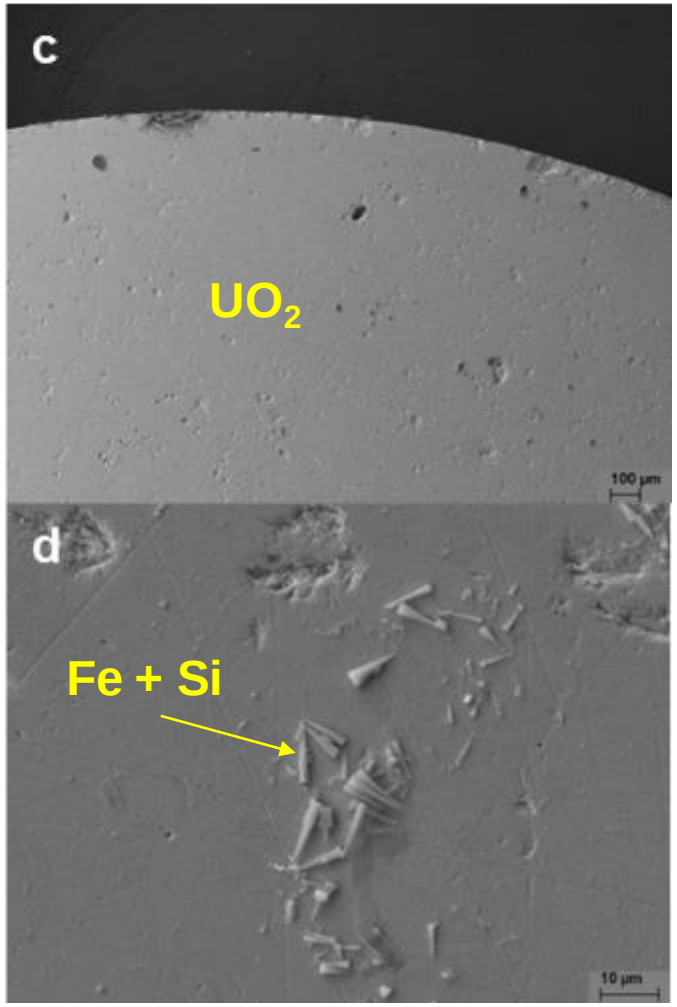
8 µm — 80% Fe, 20% Si

Lower crust

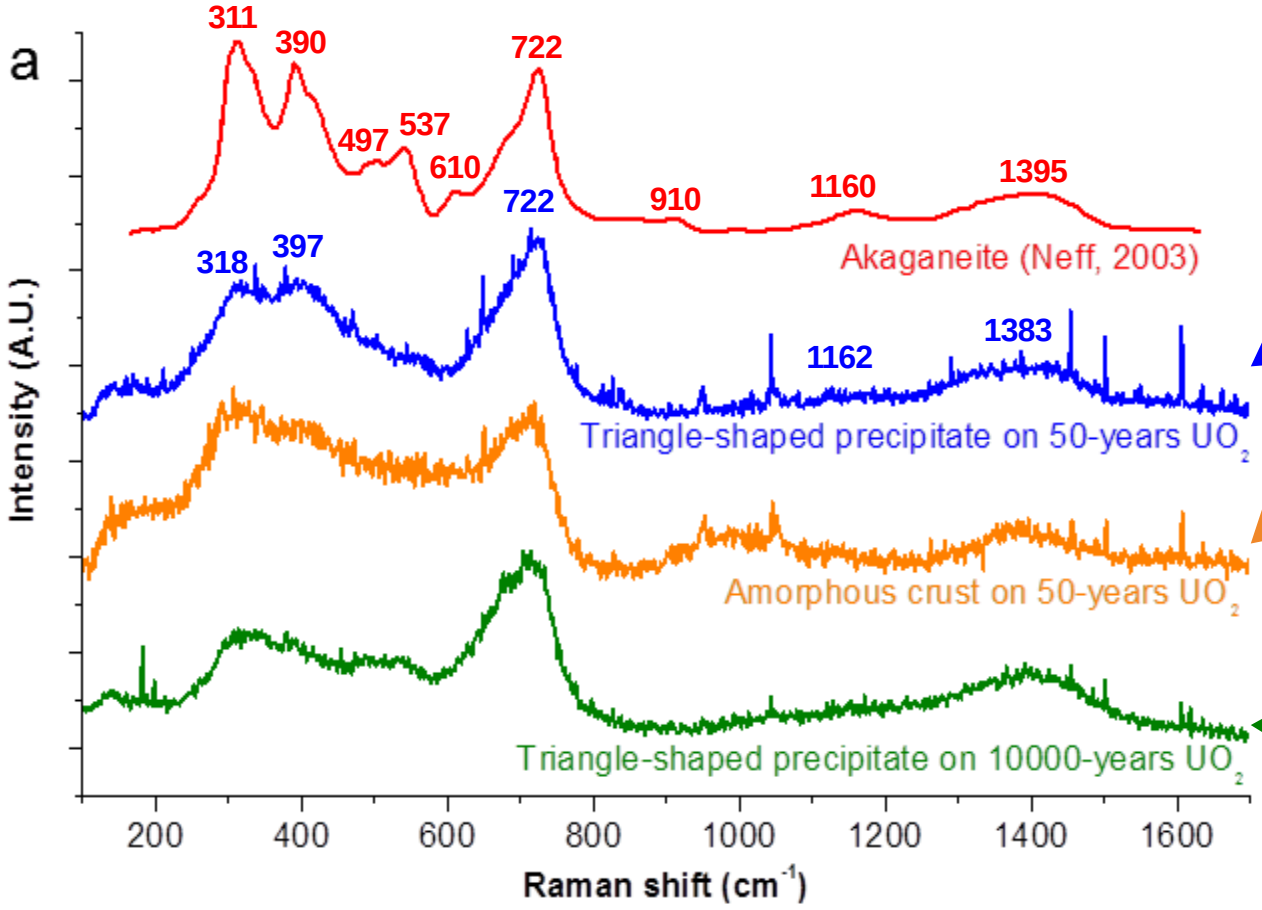
50-years UO_2

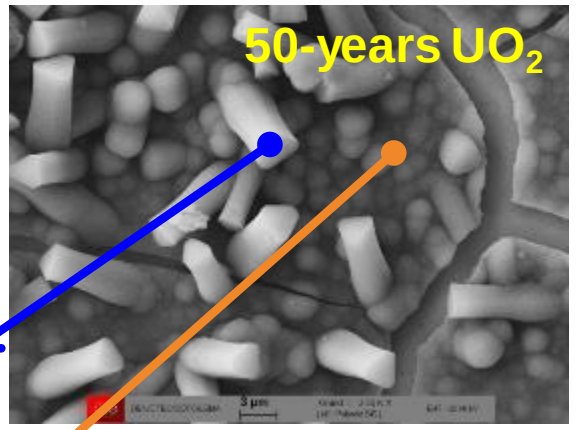
10000-years UO_2

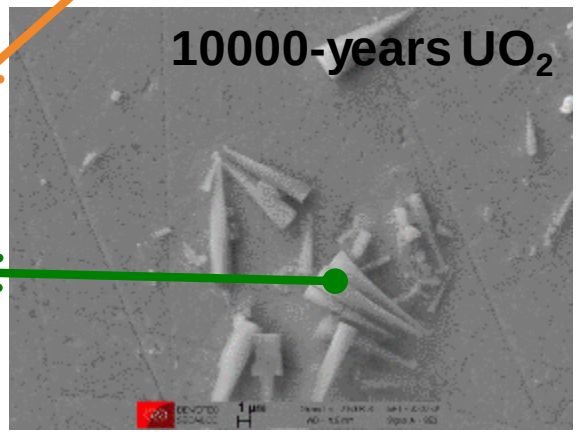




UO_2 PELLETS CHARACTERIZATIONS: RAMAN SPECTROSCOPY





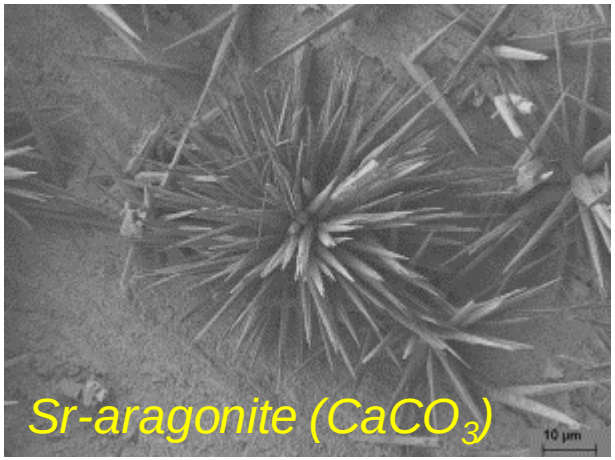


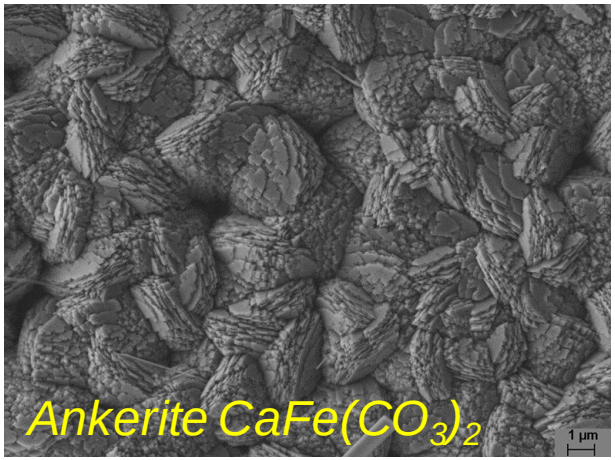
- Precipitation of the Fe(III)-oxyhydroxide : akageneite FeOOH
- Si detected by EDS → Amorphous cronstedtite $Fe^{2+}_2Fe^{3+}_2SiO_5(OH)_4$?

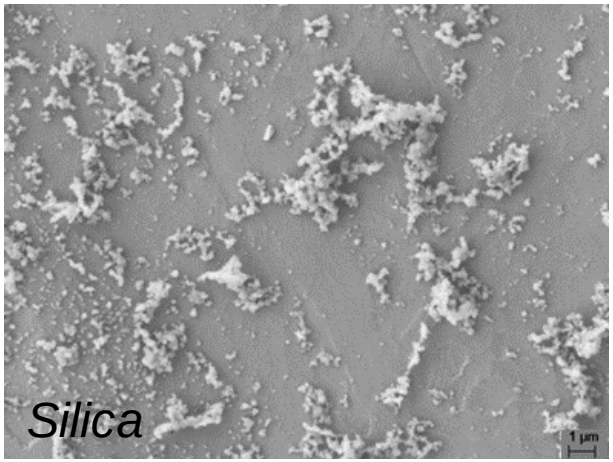
IRON FOIL CHARACTERIZATIONS: SEM

SEM images: in collaboration with G. Jouan (CEA/LEMA)
Identification by EDX and Raman spectroscopy

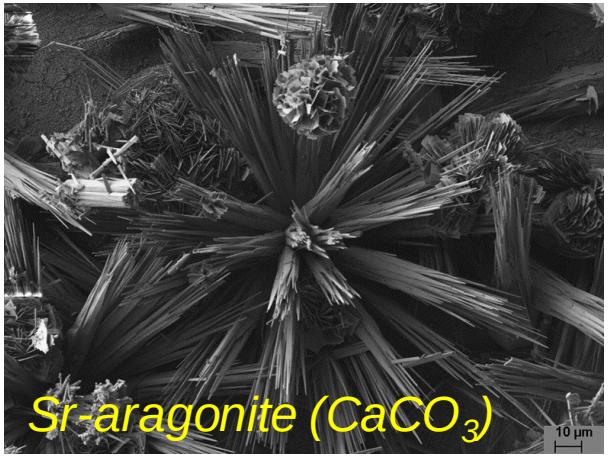
With 50-years UO_2

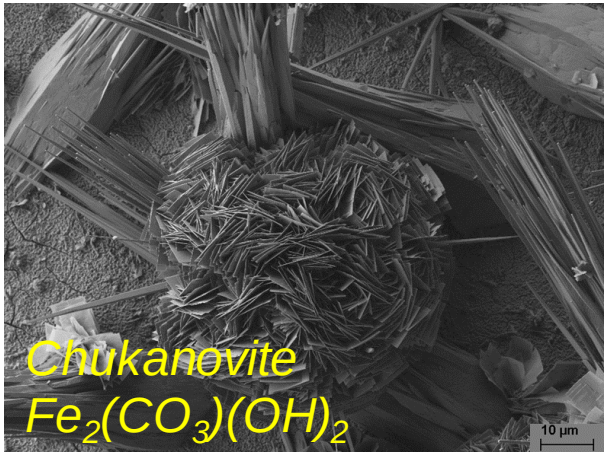


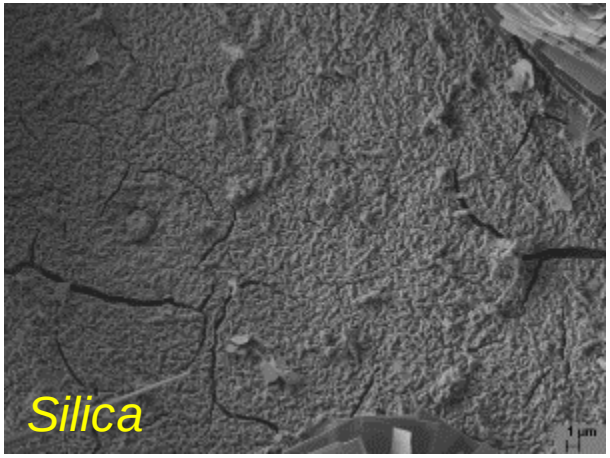




With 10000-years UO_2

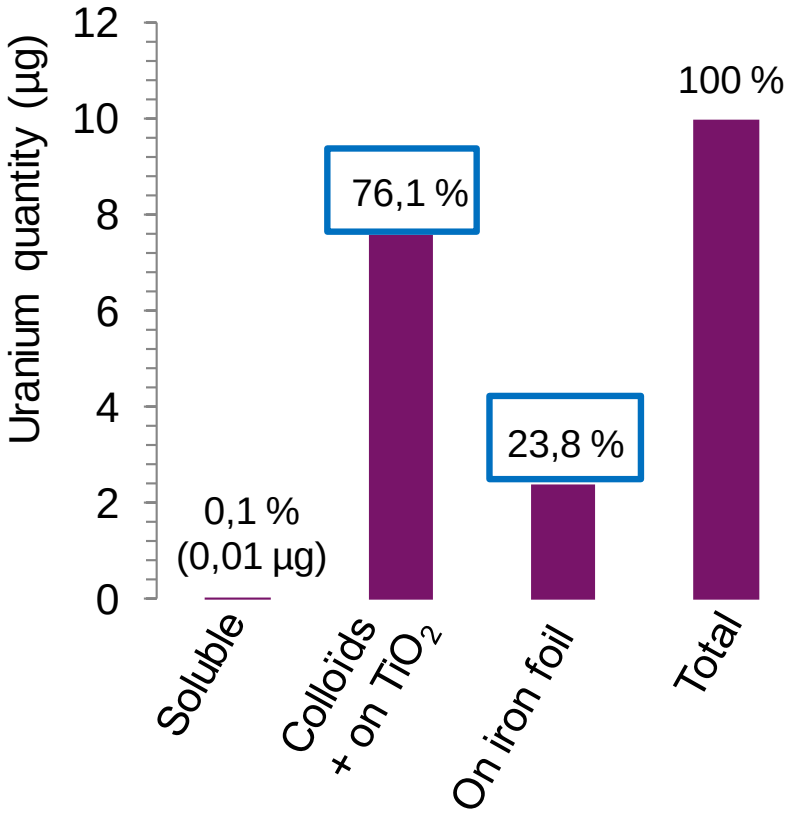






URANIUM TOTAL RELEASE

50-years UO_2

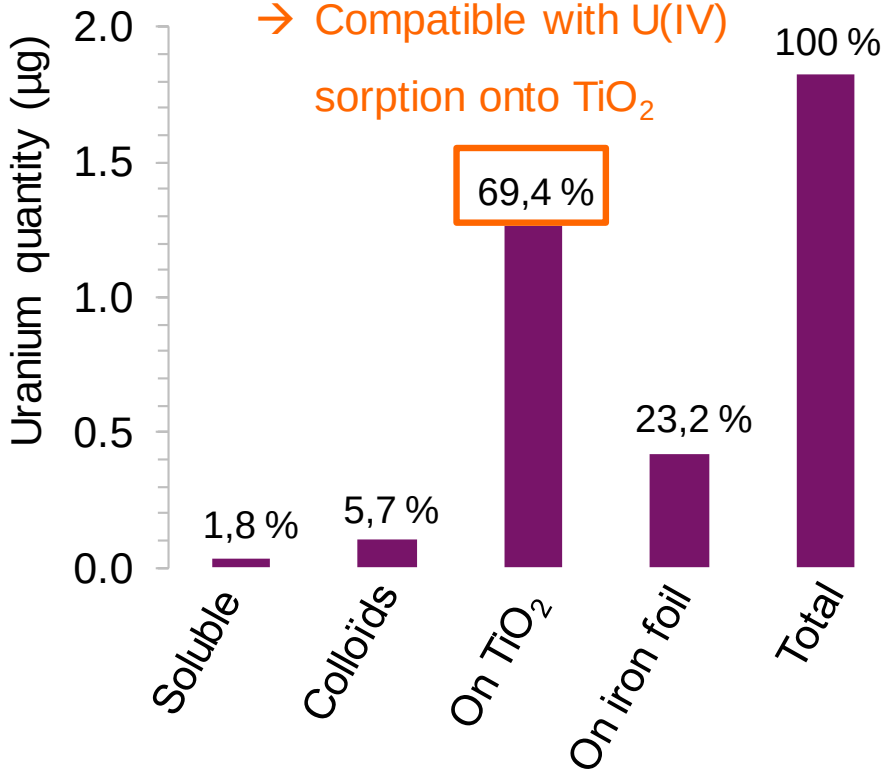


→ Only 10 µg U released

→ **Strong inhibition of the oxidative dissolution**

10000-years UO_2

→ Compatible with U(IV) sorption onto TiO_2



→ Only 2 µg U released

→ For comparison, total U released:

In carbonated water: > 1000 µg in 450 days; for 10000-years UO_2: 2 µg in 450 days

Modeling of the experiments in presence of iron

- **Main objectives** (this presentation)
  - Support the interpretation of lab experiments by modeling
  - Calibrate kinetic rate laws of UO_2 dissolution and iron corrosion from the literature
  - Develop a reactive transport model of the whole system UO_2 – Fe(0) – groundwater
- **Background goals**
  - Extend this geochemical model to spent-fuel (SF) matrix
  - Performance assessment of the disposal near field SF – steel canister – clay

Modeling approach

Geochemical thermodynamics and kinetics

- Code : **CHESS - HYTEC**
- Database: **ThermoChimie** (Andra)
  + added species (H_2O_2, Pu-doped UO_2,…)
- Added kinetic laws:

H_2O_2 production

$$\frac{d[H_2O_2(aq)]}{dt} = \frac{d[H_2(aq)]}{dt} = k_{rad}\, A_{UO_2}$$

$$k_{rad} = 10^{-9}\ mol.m^{-2}.sec^{-1}\ \left(385\ MBq.g_{UO_2}^{-1}\right)$$

H_2O_2 disproportionation

$$H_2O_2(aq) \rightarrow H_2O + 0.5O_2(aq)$$

$$\frac{d[H_2O_2(aq)]}{dt} = k_{disp}\,[H_2O_2(aq)]$$

Iron corrosion

$$Fe + 2H_2O \rightarrow Fe^{2+} + 2OH^- + H_2(aq)$$

$$\frac{d[Fe]}{dt} = k_{anox}\, A_{Fe}\ ;\ k_{anox} = 10^{-9}\ mol.m^{-2}.sec^{-1}$$

Pu-doped UO_2 dissolution

$$\frac{d[UO_2]}{dt} = R_{total} = R_{red} + R_{O_2} + R_{H_2O_2}$$

In reducing media

$$UO_2 + H_2O \rightleftharpoons U(OH)_4(aq)$$

$$R_{red} = \frac{d[UO_2]}{dt} = k_{red}\, A_{UO_2} \left(\frac{IAP}{K_{UO_2}} - 1\right)$$

$$k_{red} = 10^{-12}\ mol.m^{-2}.sec^{-1}$$

In oxidizing media

H_2O_2

$$UO_2 + 2H^+ + H_2O_2(aq) \rightarrow UO_2^{2+} + 2H_2O$$

$$R_{H_2O_2} = \frac{d[UO_2]}{dt} = k_{ox}^{H_2O_2}\, A_{UO_2}\, (H_2O_2(aq))^{0.59}$$

$$k_{ox}^{H_2O_2} = 10^{-6}\ mol.m^{-2}.sec^{-1}$$

O_2

$$UO_2 + 2H^+ + 0.5O_2(aq) \rightarrow UO_2^{2+} + H_2O$$

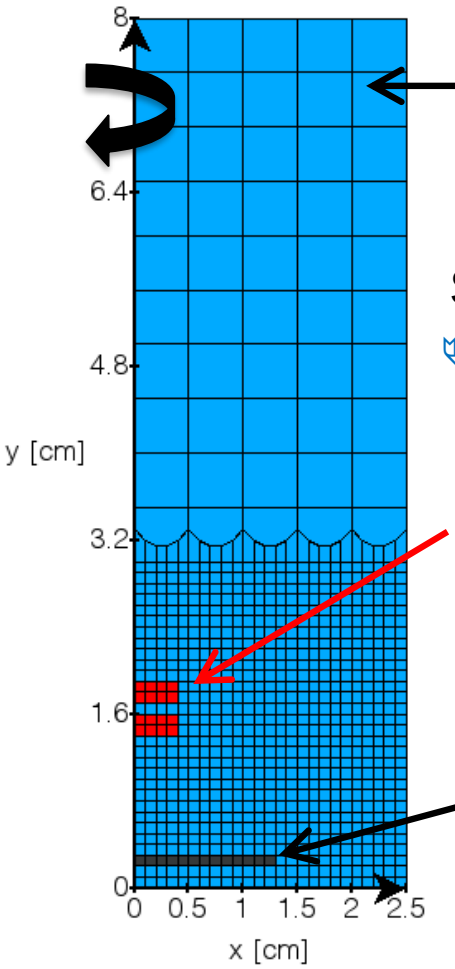
$$R_{O_2} = \frac{d[UO_2]}{dt} = k_{ox}^{O_2}\, A_{UO_2}\, (O_2(aq))^{0.74}$$

$$k_{ox}^{O_2} = 10^{-7}\ mol.m^{-2}.sec^{-1}$$

Modeling approach

Reactive transport

Modeling grid



Cylindrical modeling grid

Synthetic COx water

↳ **To simulate the COx porewater chemistry**

Two Pu-doped UO_2 pellets
(α activity = 385 $MBq.g_{UO2}^{-1}$)

↳ **To simulate a 50 years old spent fuel**

Iron foil

↳ **To simulate the steel overpack**

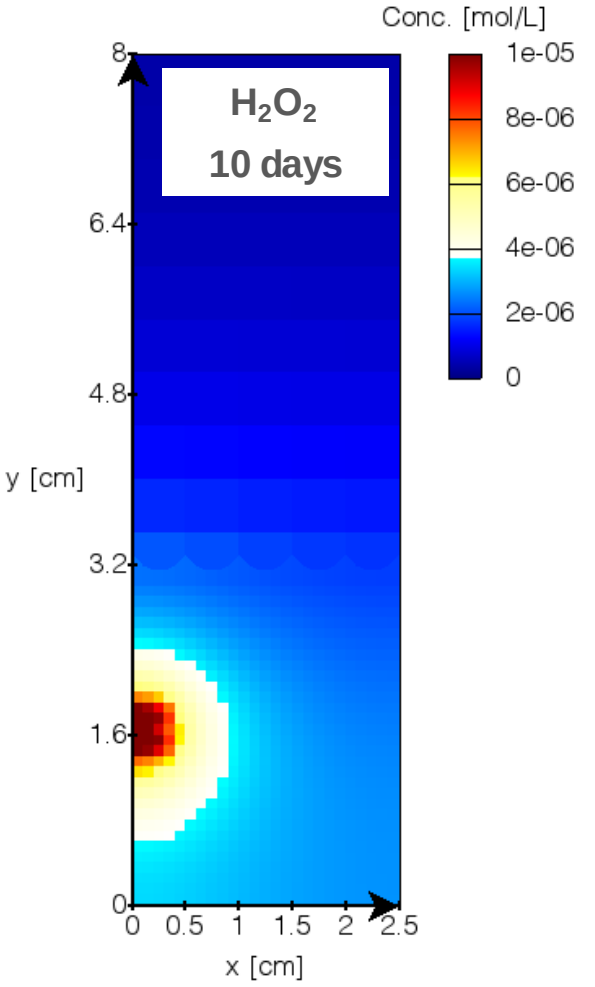
No stirring during lab test
=> diffusion and coupling

$$\frac{\partial \omega c_i}{\partial t} = \nabla(D_e.\nabla c_i) - \frac{\partial \omega \bar{c}_i}{\partial t}$$

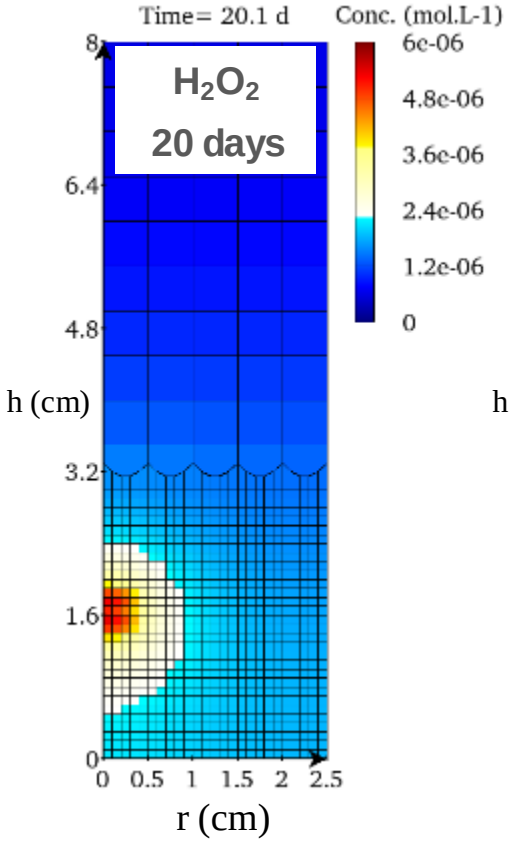
Modeling of lab test

Diffusion of H_2O_2 vs. diffusion of Fe^{2+}

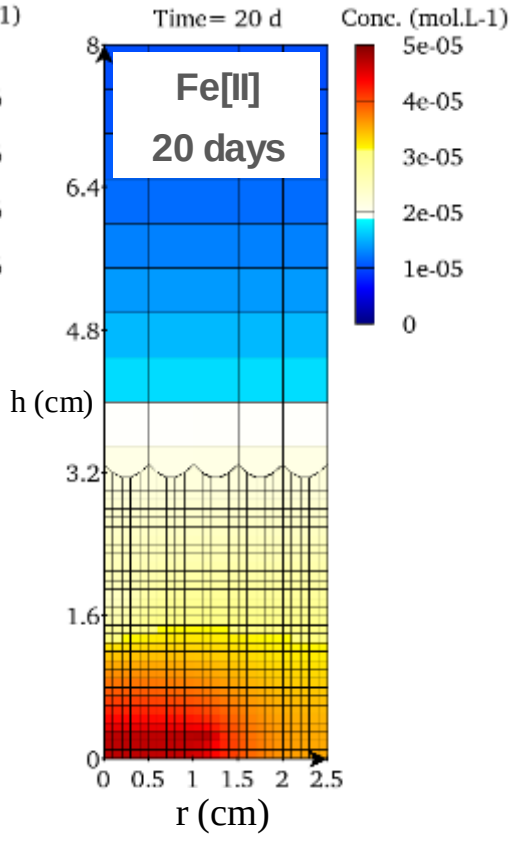
H_2O_2 initial production



H_2O_2 production and disproportion

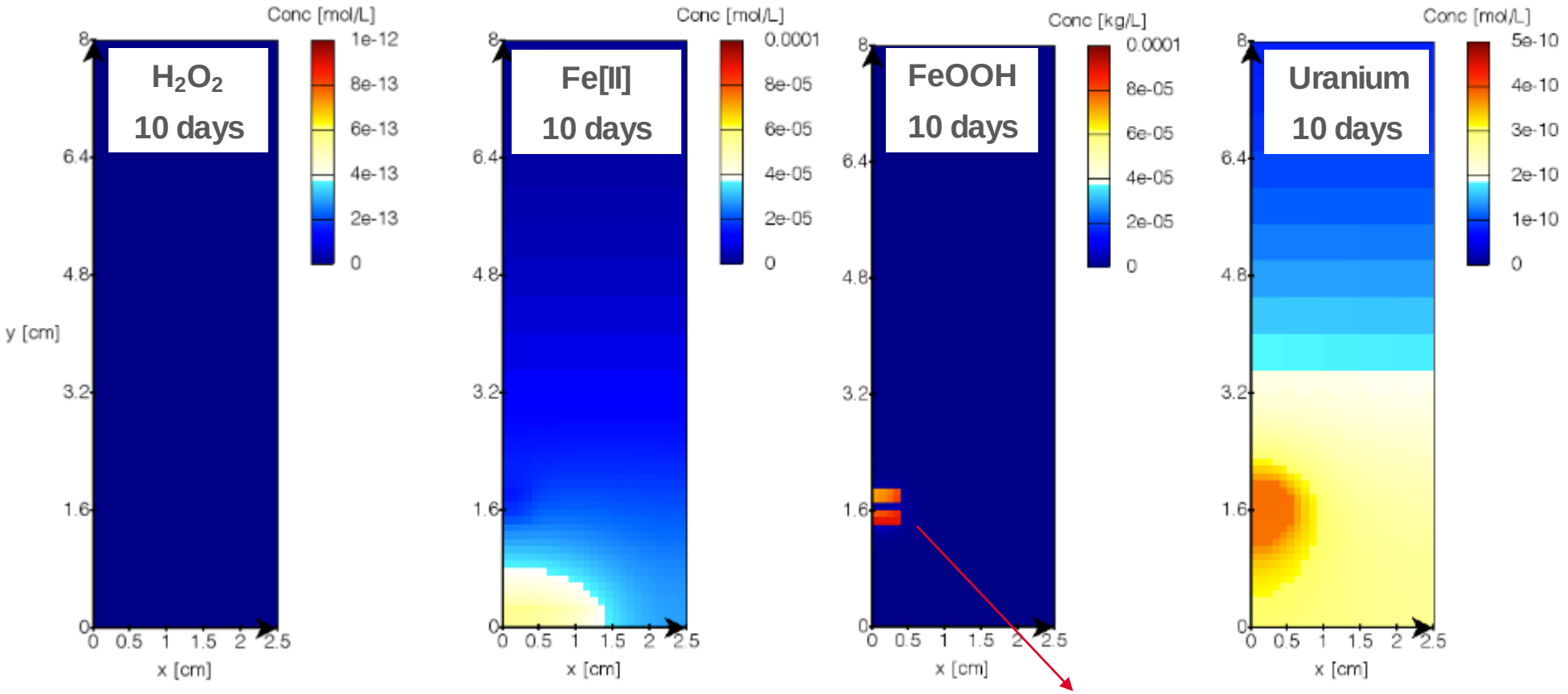


Fe^{2+} production (anoxic iron corrosion)

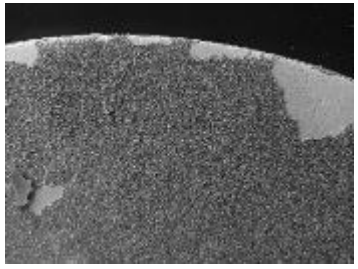


50-YEARS UO_2 MODELING RESULTS : FE(III)-HYDROXIDE PRECIPITATION

Reaction H_2O_2 / Fe^{2+} at the UO_2 surface



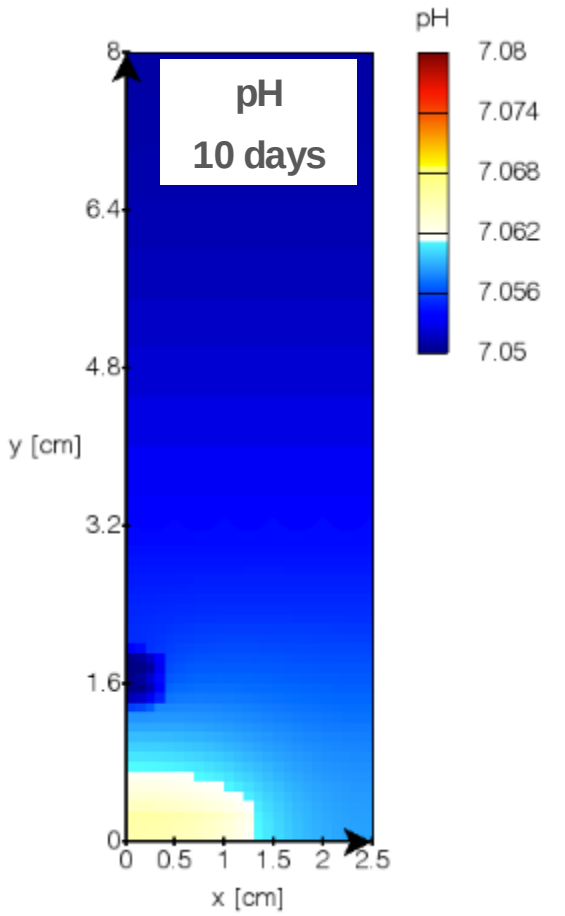
$\frac{1}{2}\ H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^-$

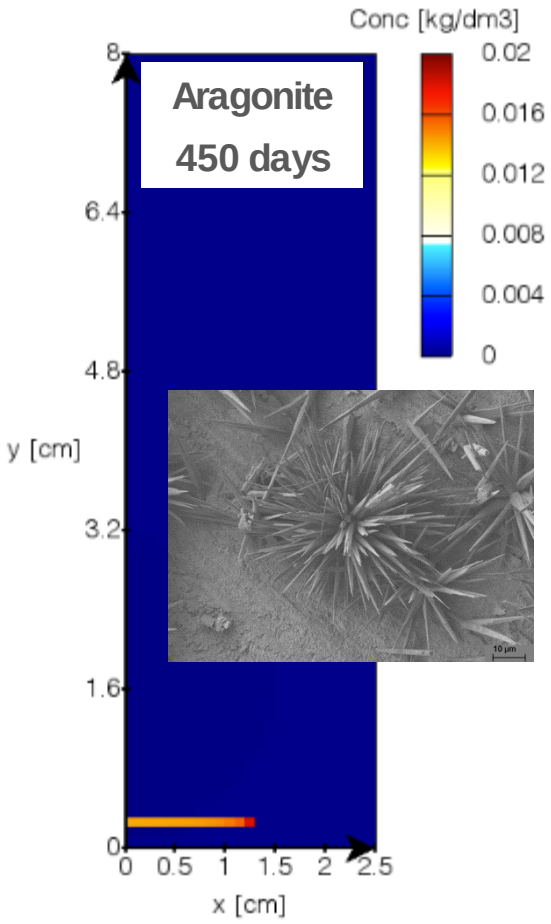


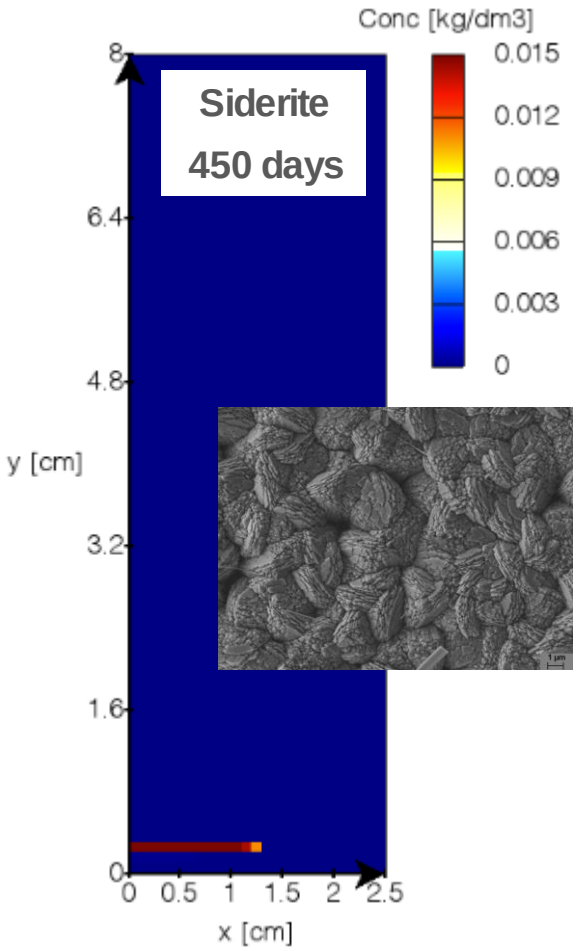
$Fe^{3+} + 2\ H_2O \rightarrow FeOOH + 3\ H^+$

50-YEARS UO_2 MODELING RESULTS: CARBONATES PRECIPITATION

Corrosion products on the iron foil surface







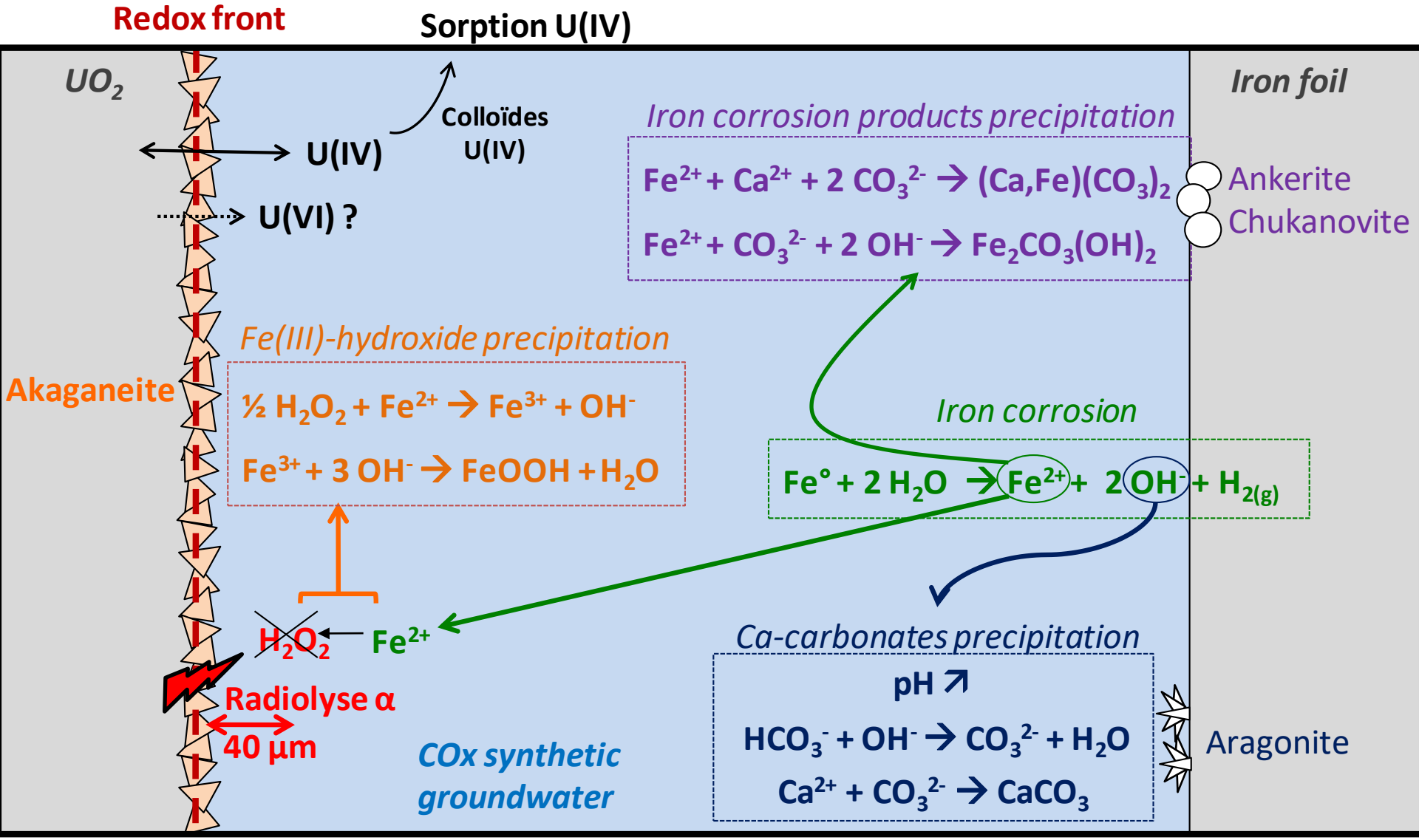
$Fe° + 2\ H_2O \rightarrow Fe^{2+} + 2\ OH^- + H_{2(g)}$

$HCO_3^+ + OH^- \rightleftharpoons CO_3^{2-} + H_2O$

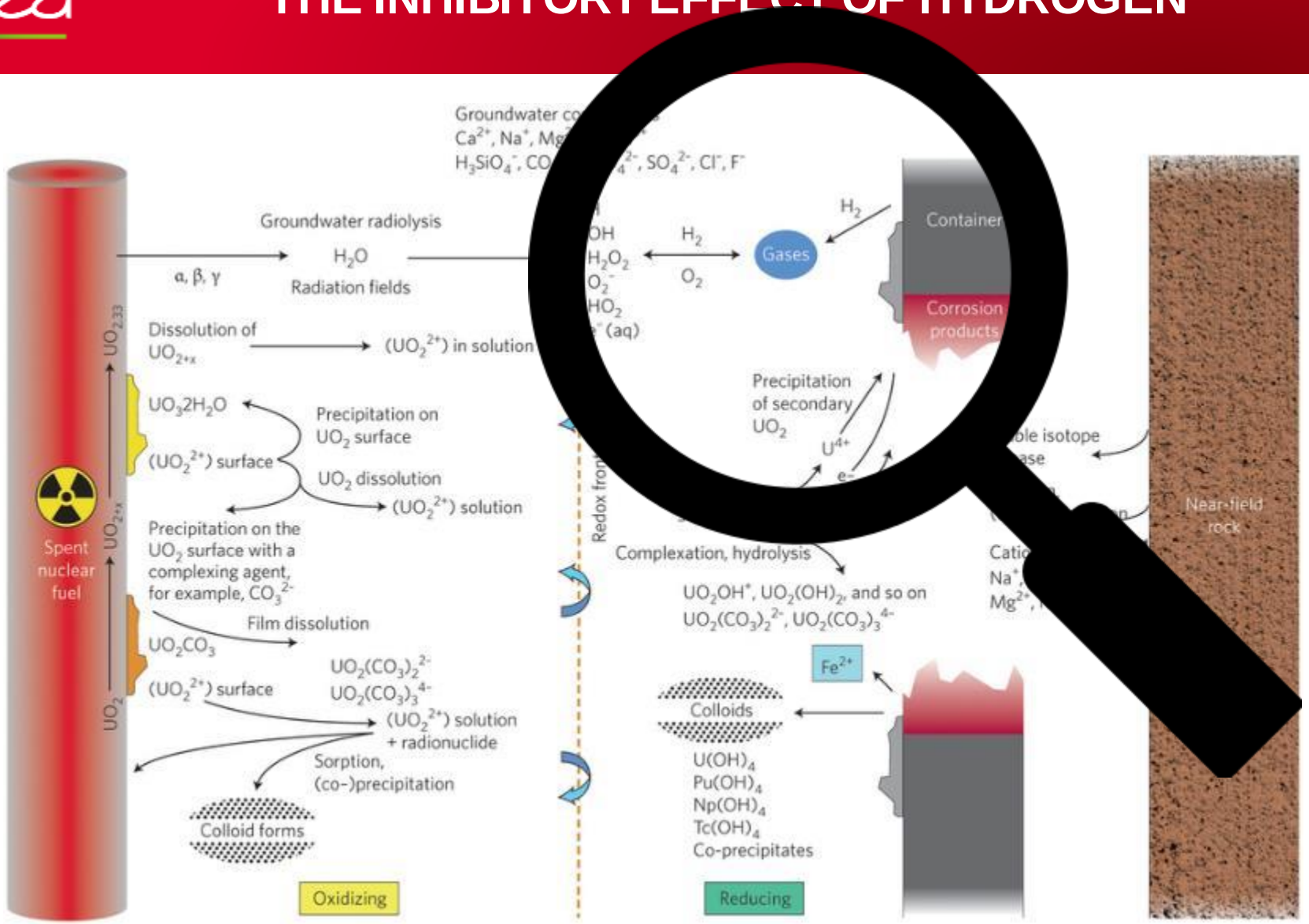
$Ca^{2+} + CO_3^{2-} \rightleftharpoons$ calcite

$Fe^{2+} + CO_3^{2-} \rightleftharpoons$ siderite

50-YEARS UO_2 MATRIX DISSOLUTION IN COX WATER IN THE PRESENCE OF IRON



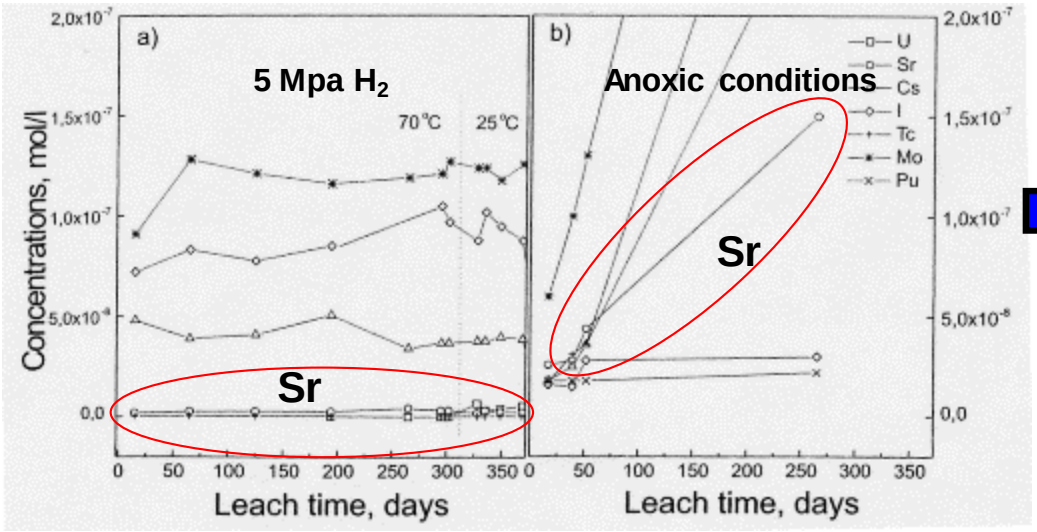
THE INHIBITORY EFFECT OF HYDROGEN



•**Rodney C. Ewing**
Nature Materials 2015

Effects of hydrogen on SF matrix dissolution

A strong inhibition of the alteration is observed…

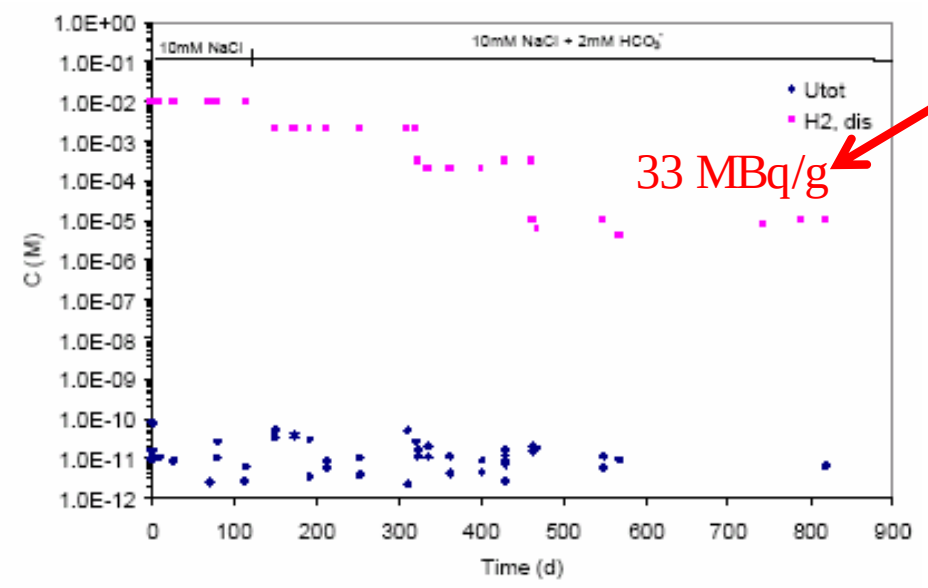


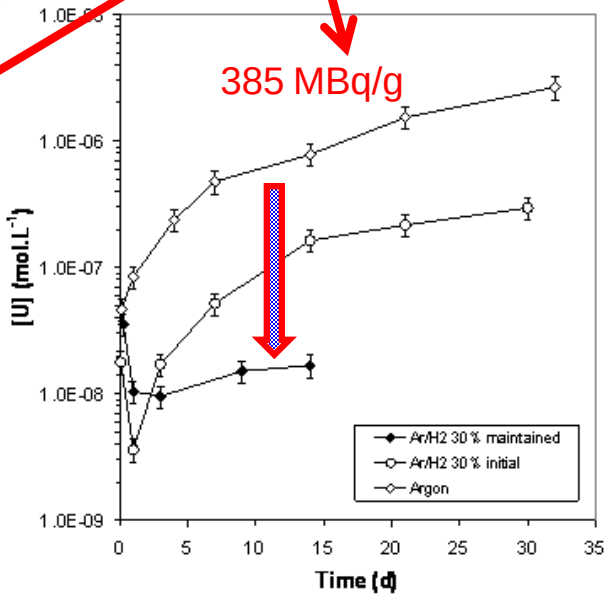
$$Fe(s) + H_2O \Leftrightarrow Fe_3O_4(s) + H_2(g)$$

Spent fuel RCA 2000 Spahiu et coll.

Chemical composition and radiation field are different

Alpha doped samples





SFS – WP3 – $^{233}UO_2$ 10 %

Radiolytically produced O_2 >> measured O_2

Muzeau et al., J. of Alloys and Compounds 2009

Which Mechanisms are Involved in this inhibitory effect ?

Key issues = catalytic decomposition of hydrogen at low temperature and is the H_2 reduction effect possible even in the long-term perspective of the SF disposal ?

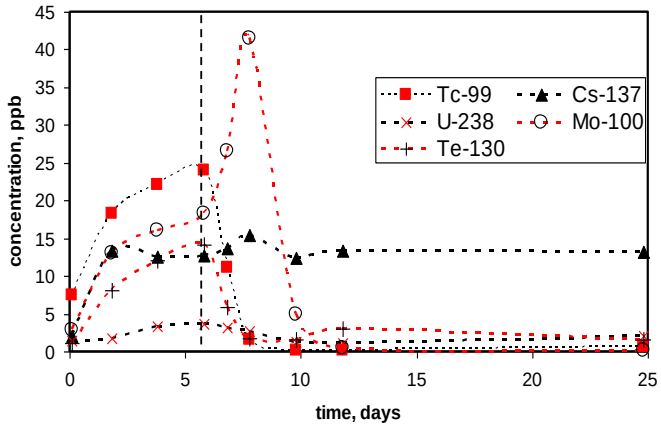
- Hydrogen activation by the $\beta\gamma$ irradiation field : $OH° + H_2 \Rightarrow H_2O + H°$

Under geological disposal

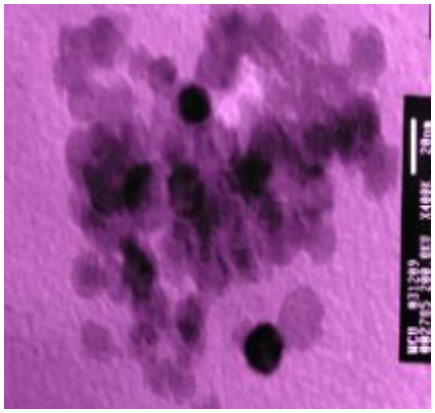
- **Hydrogen activation by the surfaces**
  - UO_2 surface + alpha Irradiation

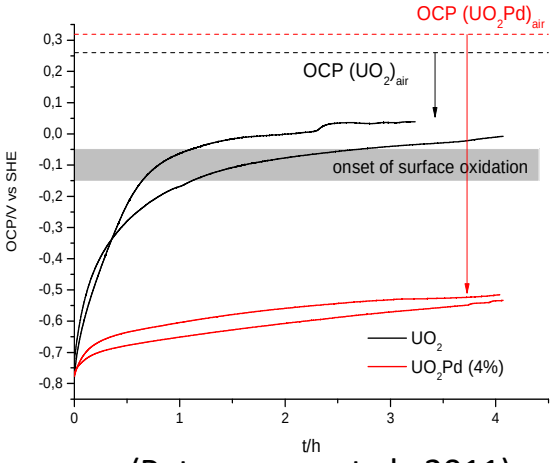
(Carbol et coll. GCA 2009 ; Bruno and Spahiu Applied geochemistry 2014)

- Epsilon Phases => Strong catalytic power



Cui et al., JNM 2011



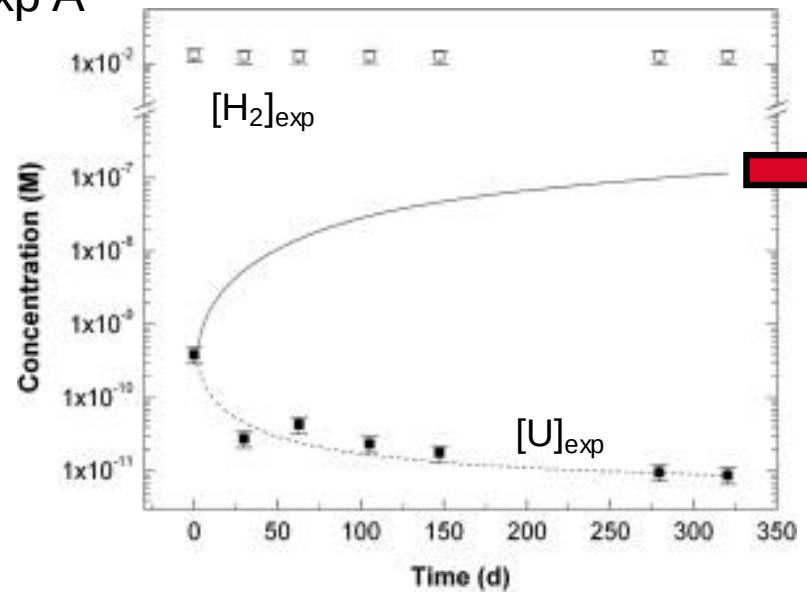


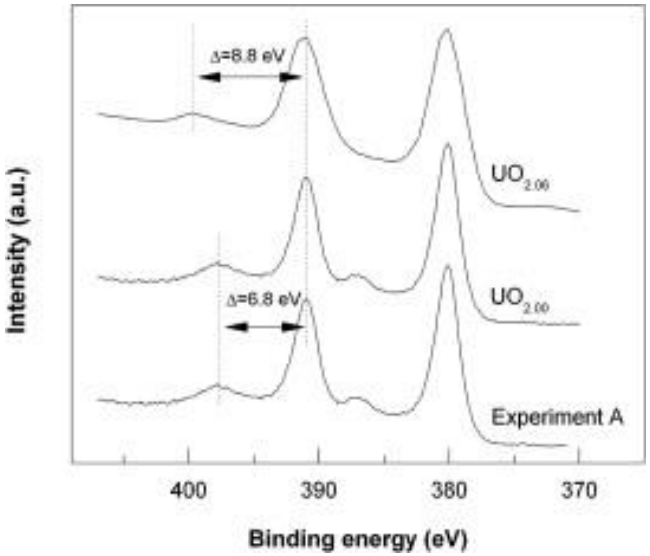
(Petersmann et al., 2011)

- OH° radical formation by the catalytic decomposition of H_2O_2 at the surface

Hydrogen suppresses UO_2 corrosion

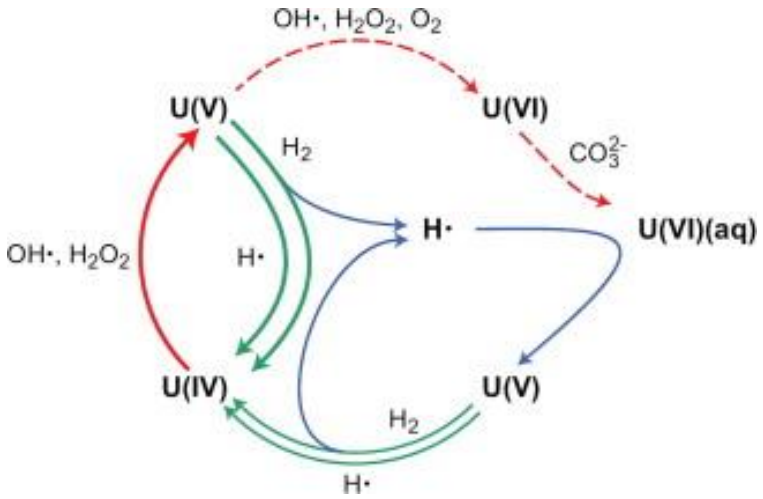
Exp A





Alpha doped UO_2 - 33 MBq/g

The expected increase in U concentration, assuming that all radiolytic oxidants oxidize the fuel surface



GCA Carbol et coll. 2009

OUTLINES

- Introduction

- Spent Fuel Corrosion processes under geological disposal

  - SF evolution and Radionuclides source terms

  - Spent fuel matrix alteration mechanisms : UOX fuel case

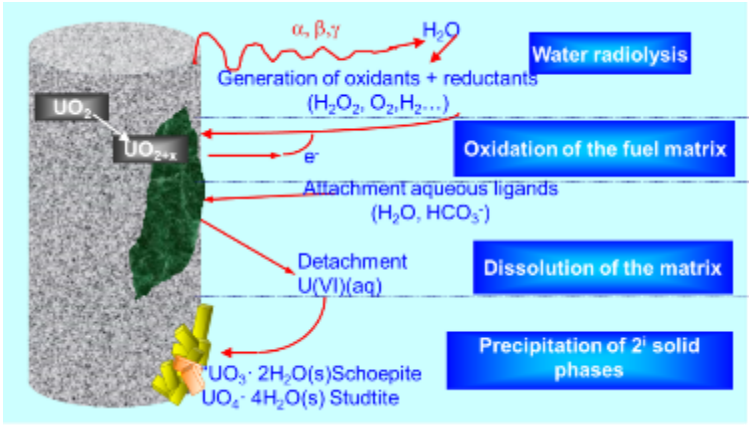
  - **Spent fuel matrix alteration mechanisms : MOX fuel case**

- Spent Fuel Corrosion processes under long term interim storage

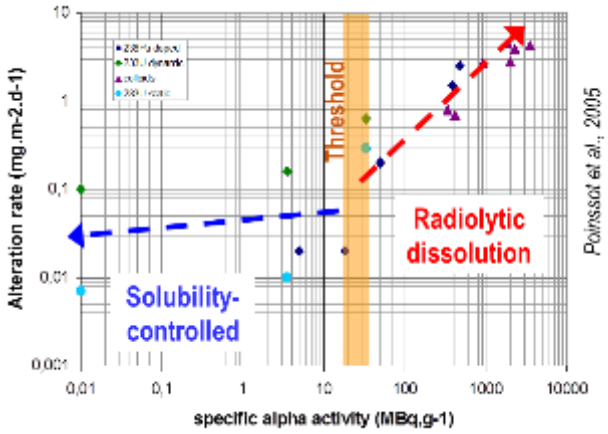
- Conclusion

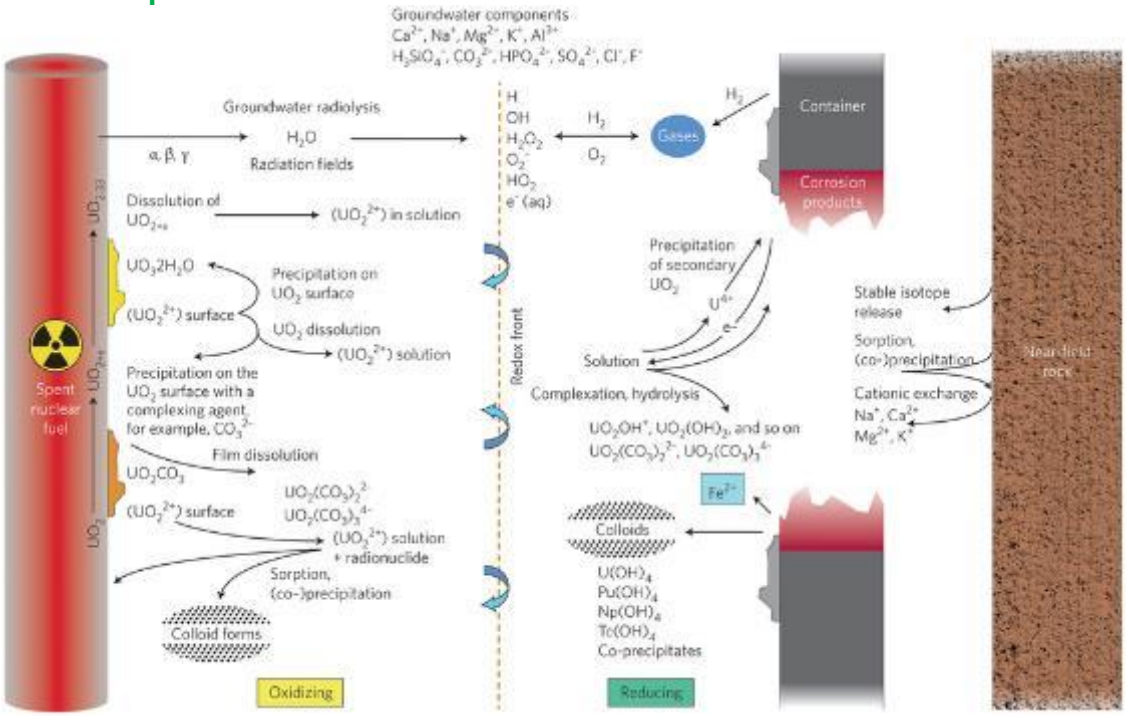
What about MOX fuels ?

There is already a broad international consensus on the corrosion mechanisms of the UOX spent fuel matrix



European Project SFS - 2005





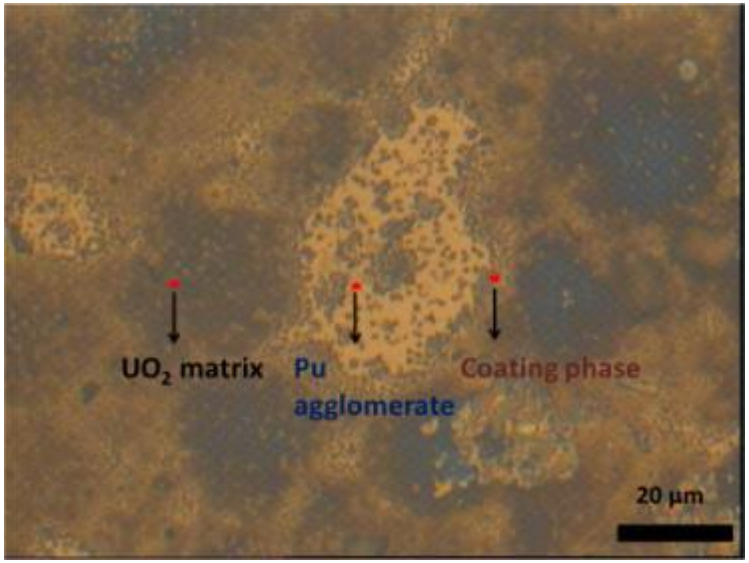
"The spent mixed-oxide fuel is not entirely the same as irradiated UO_2, but the processes of corrosion and alteration will be similar to that described here for irradiated UO_2. "

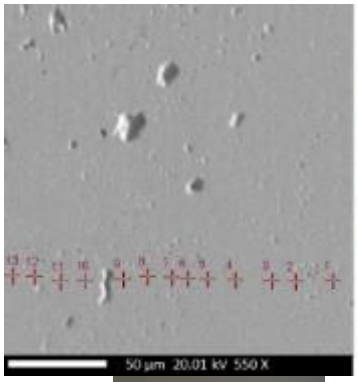
•Rodney C. Ewing
Nature Materials 2015

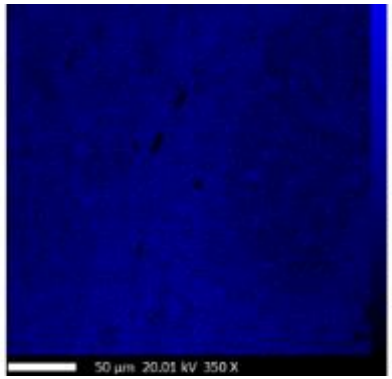
Can we really extend these concepts to the case of MOX fuel and should we take into account certain specificities ?

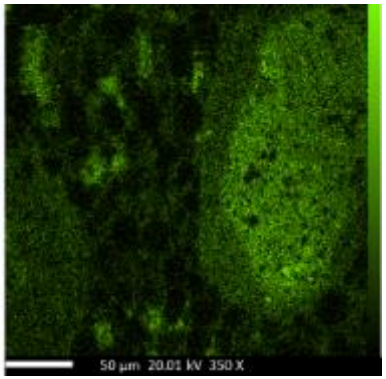
The French Mimas Mox fuel - Before irradiation

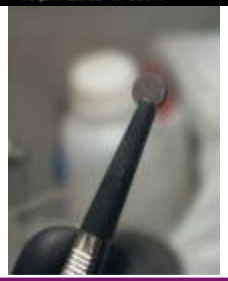
Fabrication: MIMAS (Micronized- MASter blend) – February 2000 – Melox facility







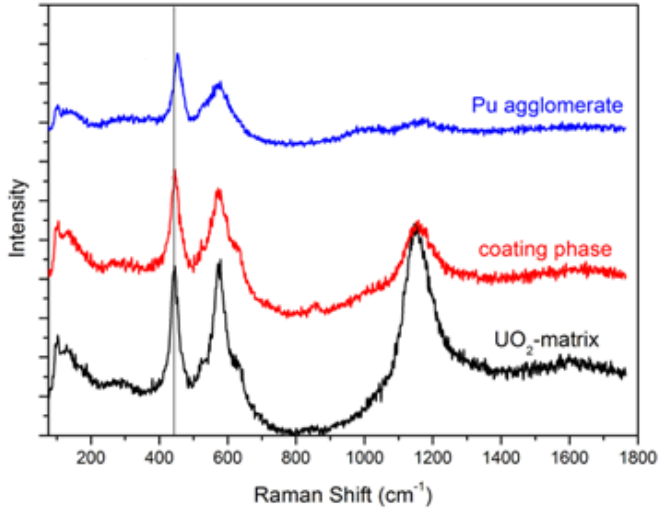




(Ammonium Di-Uranate powders) type UO_2 powders

MOX 7.5 wt.%

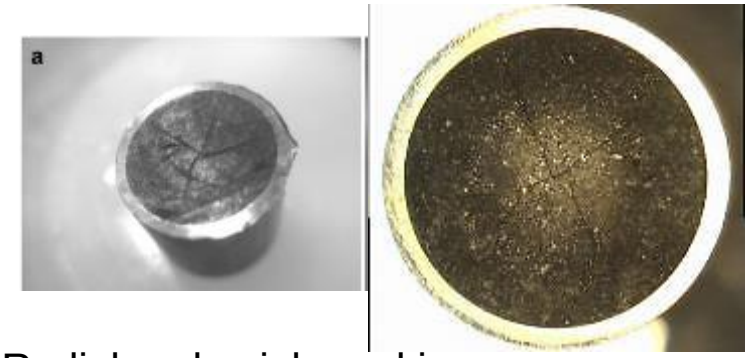
	[Pu] wt.%	Total amount (%)	Surface fraction (%)
Pu agglomerate	20	40	11
Coating phase	7,3	45	42
UO_2 matrix	2,7	15	47



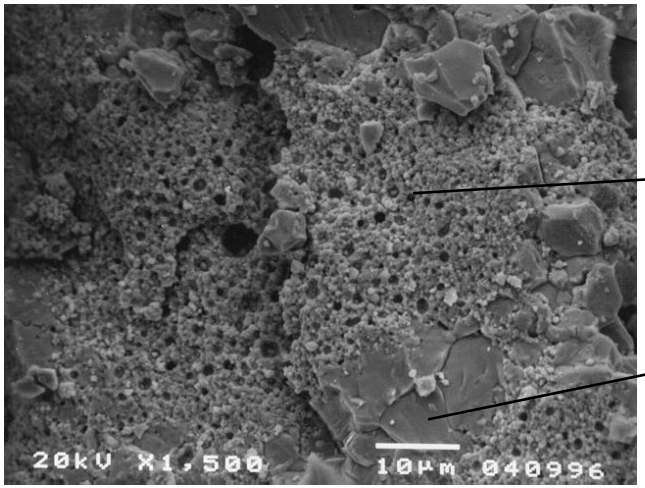
MIMAS MOX fuels are characterized by complex microstructure with plutonium-bearing aggregates having high Pu concentrations (20%) and by the existence other zones with lower concentrations (2 to 7%)

The French Mimas Mox fuel - After irradiation

MOX spent fuel – Mimas ADU - Dampierre 2 – 4 cycles – 47.7 GWd/t



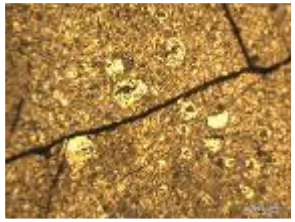
Radial and axial cracking



Local BU =130 Gwd/t

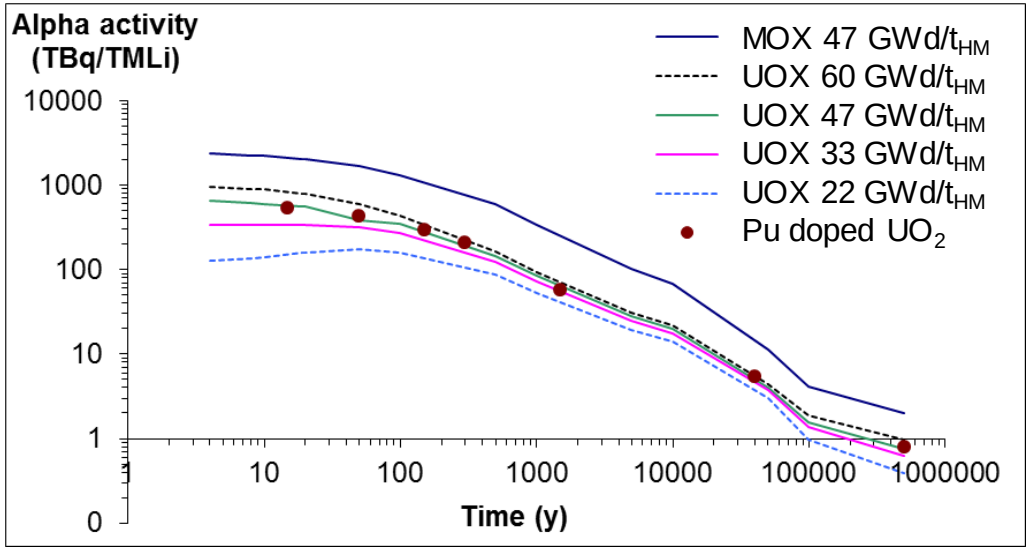
15 to 18 % Pu

3 % Pu



A restructuring of plutonium enriched agglomerates is observed (submicronic grains and high porosity - HBS)

The alpha activity remains higher than for UOX



The Experimental approach

A step by step approach including gradually the influence of the environment on the oxidative dissolution of MOX fuel under water radiolysis was developed

Leaching experiments under static and anoxic conditions, T = 25°C

MOX 7.5 wt.%

MOX 47 GWd/t

Carbonated water

Synthetic Callovian-Oxfordian (COx) water

Synthetic Callovian-Oxfordian (COx) water and corroded iron to simulate the steel overpack

chemical and radiochemical analyzes + characterization of surfaces by EPMA, SEM, Raman ...

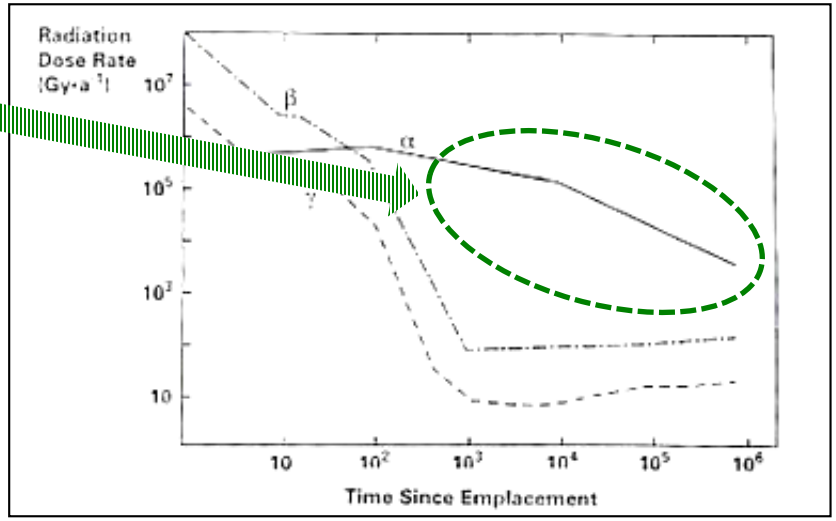
Eh and pH measurements

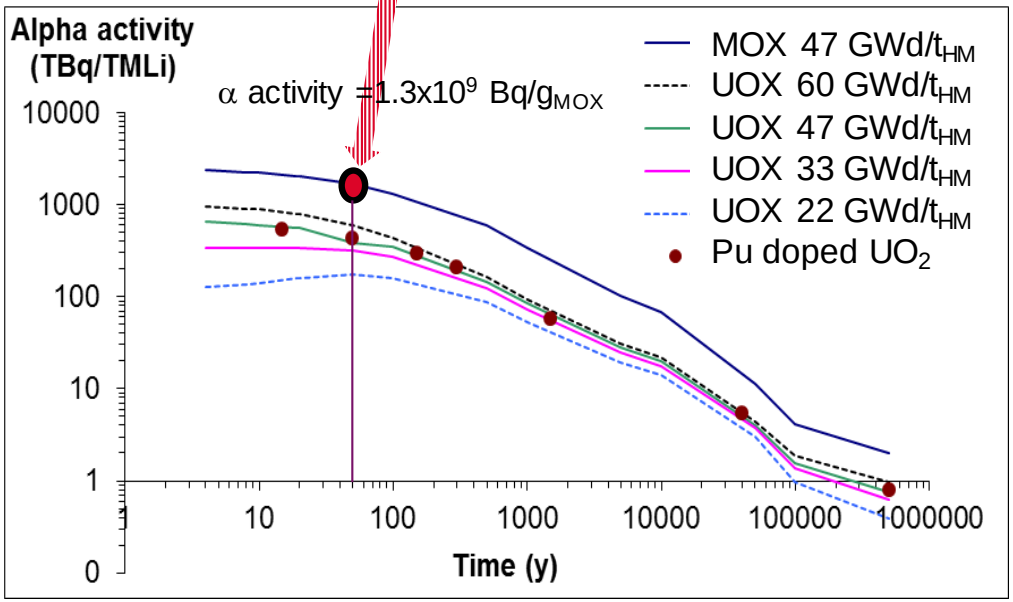
Why to study the unirradiated material ?

MOX 7.5 wt.%

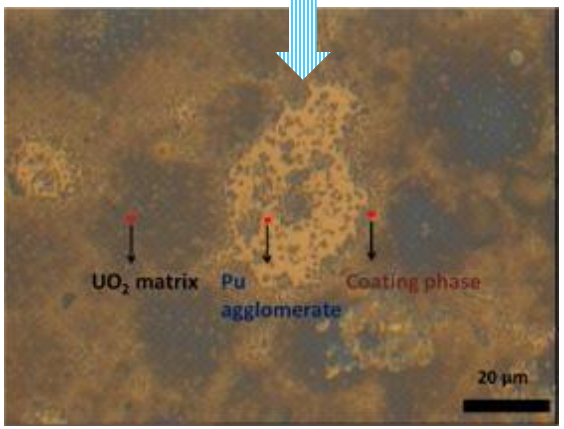
This unirradiated MOX **is mainly alpha emitter** that is worth for geological disposal studies

Its alpha activity is high thereby amplifying the mechanisms of alteration => it helps to study the influence of the environment on the oxidative dissolution under alpha radiolysis "alone"



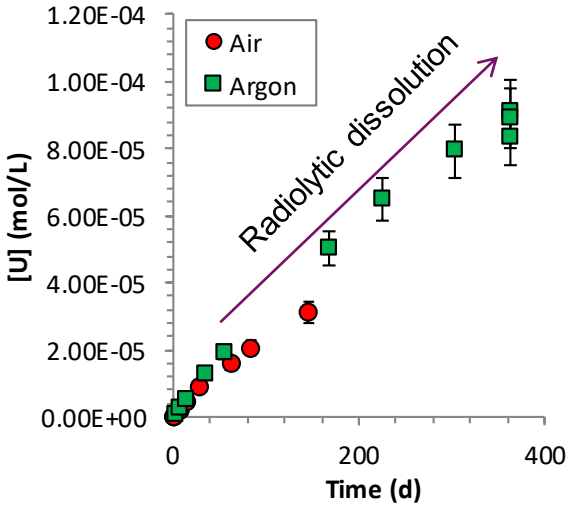


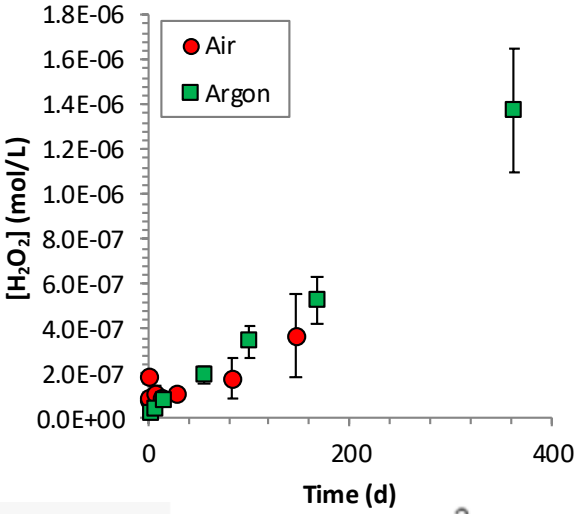
It is possible to study the influence of the chemical and microstructural heterogeneities

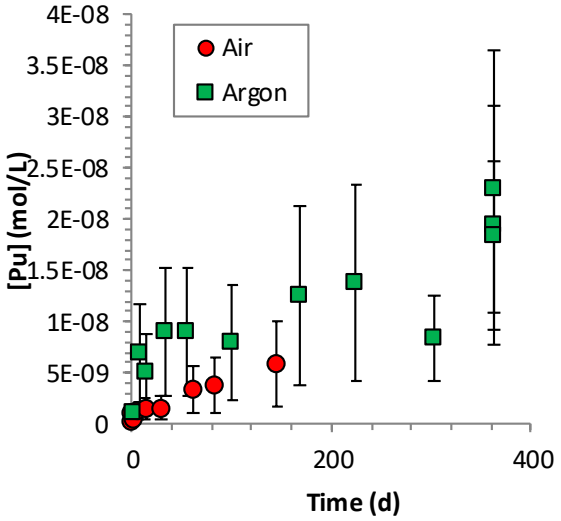


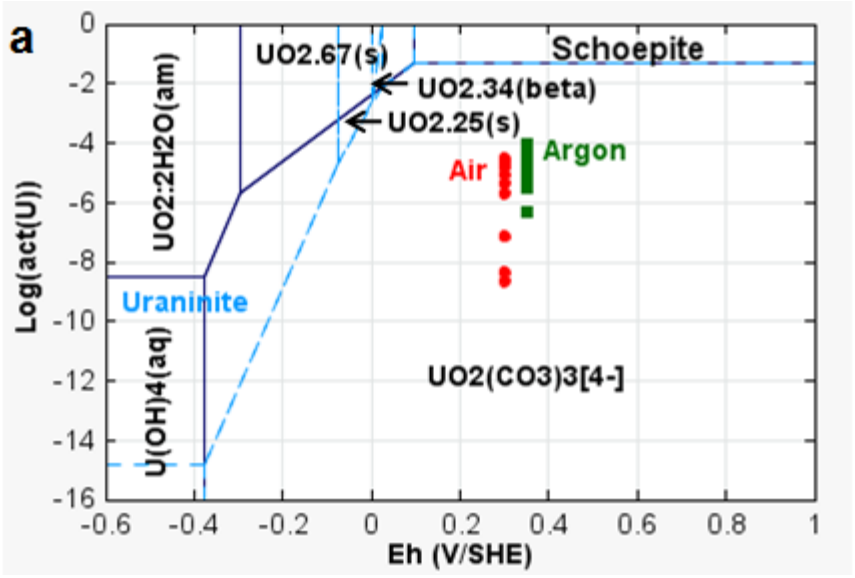
The oxidative dissolution of un-irradiated MOX 7.5 wt.%

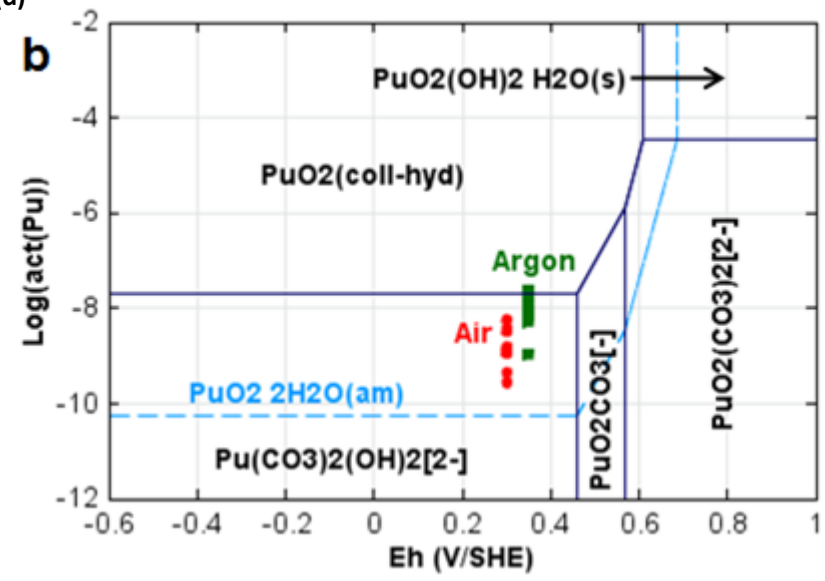
Carbonated water 10^{-2}M



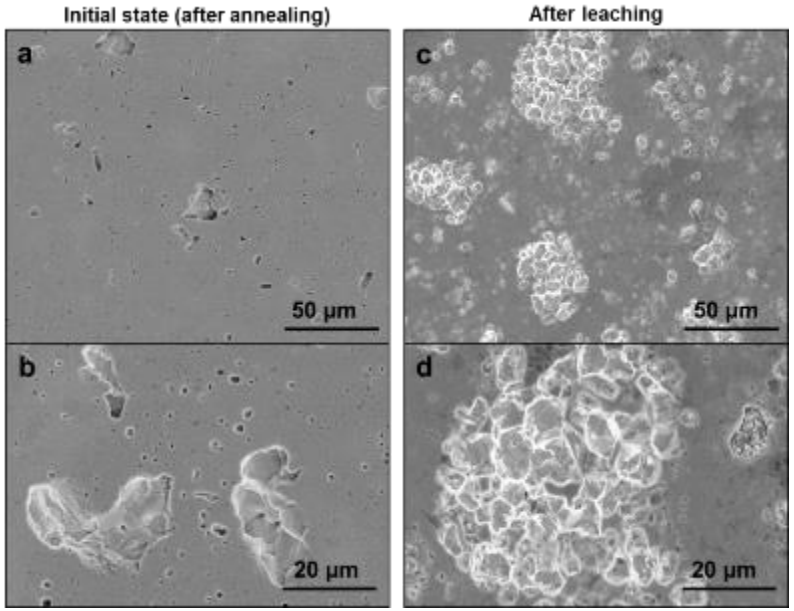


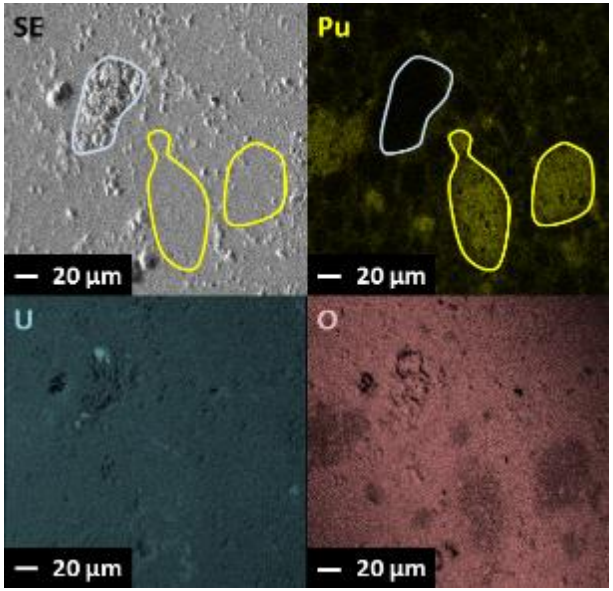


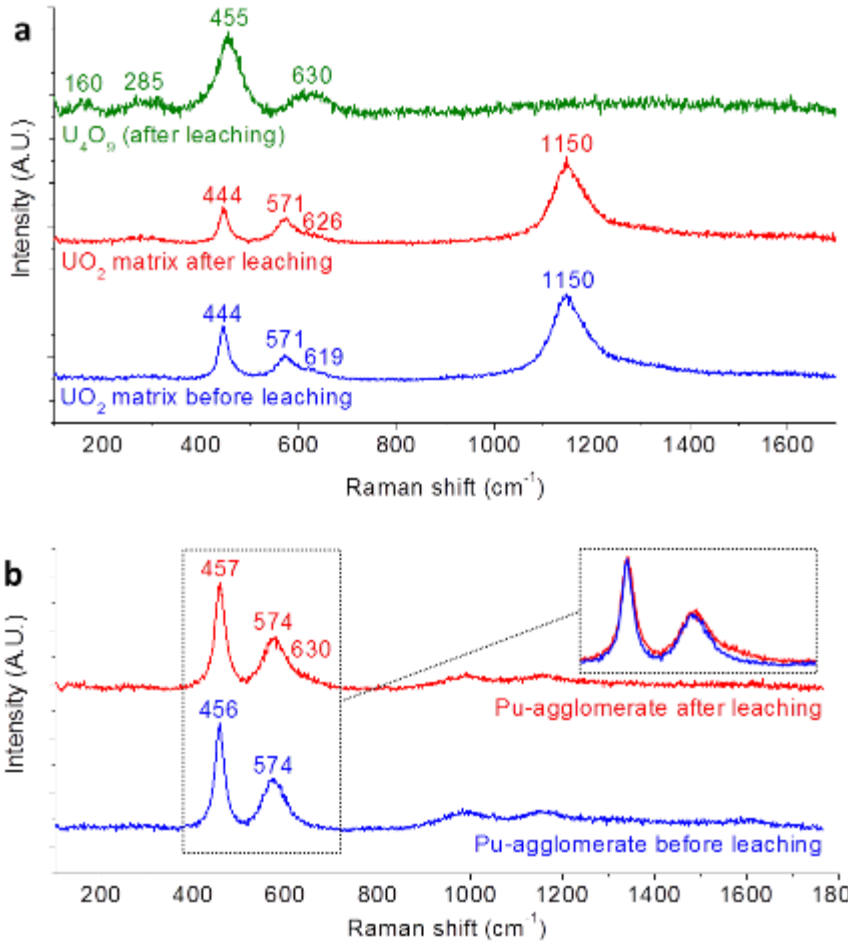




The oxidative dissolution of un-irradiated MOX 7.5 wt.%



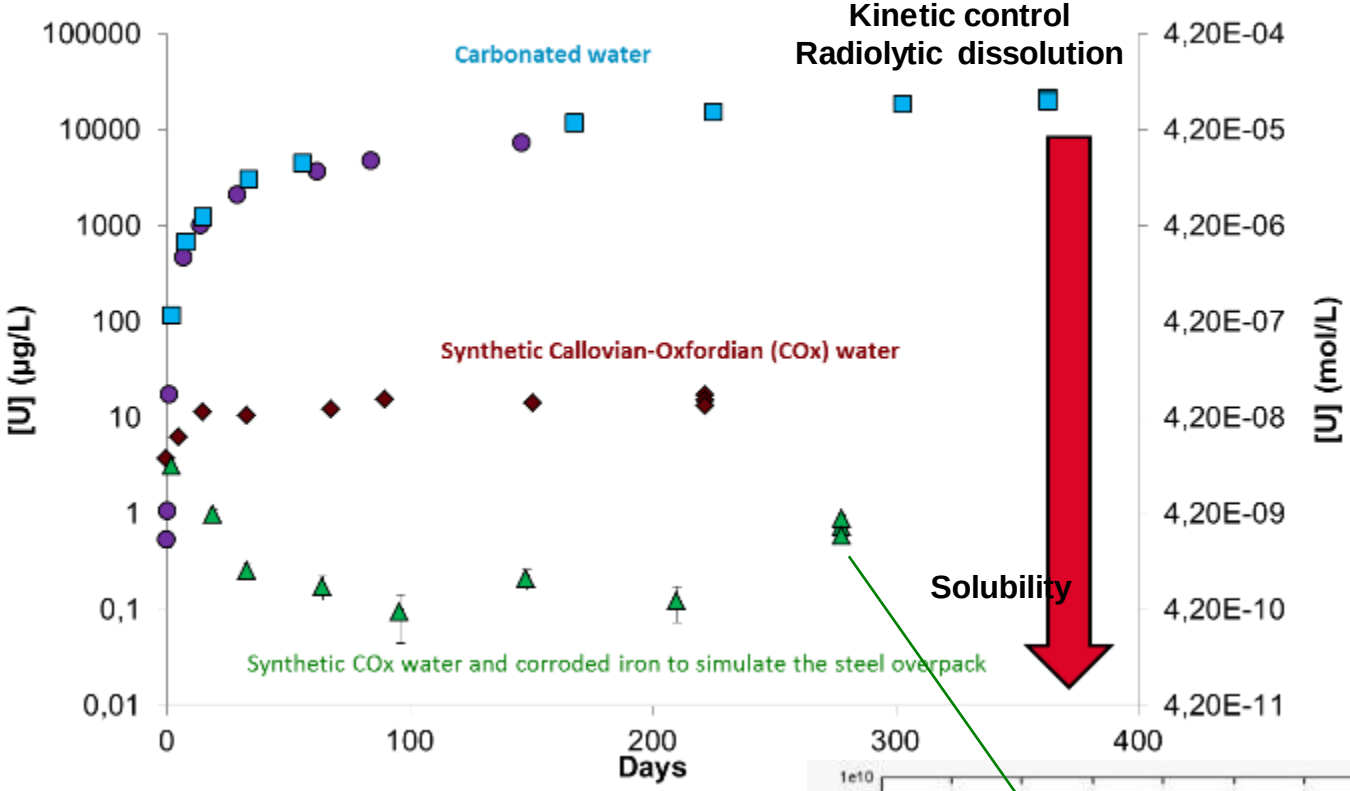




- Surface characterizations (SEM, EPMA) of the MOX pellets after leaching indicate a preferential dissolution of the UO_2 matrix compared to Pu-enriched agglomerates

- The presence of carbonates did not enable observation of an oxidized layer by Raman spectroscopy with the exception of a few areas revealing the presence of U_4O_9

Consideration of the environment on the oxidative dissolution of MOX7.5 wt.%



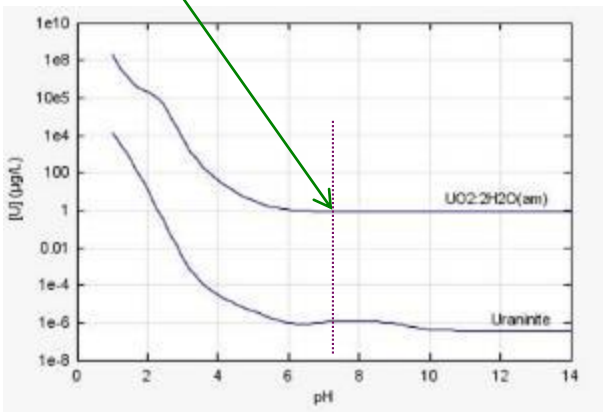
Redox (exp)

+320±30 mV/ESH

-150±30 mV/ESH

H_2 4000 ppm

An evolution from a kinetic control (radiolytic dissolution) to a solubility controlled regime is clearly observed for the MOX



NEA data

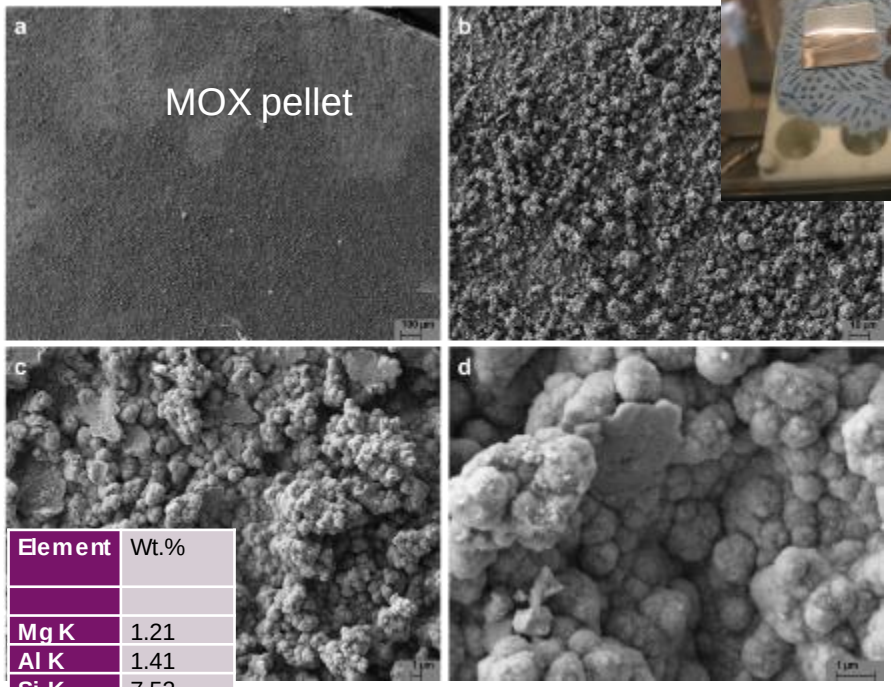
<u>To what extent the presence of iron inhibits the oxidative dissolution ?</u>

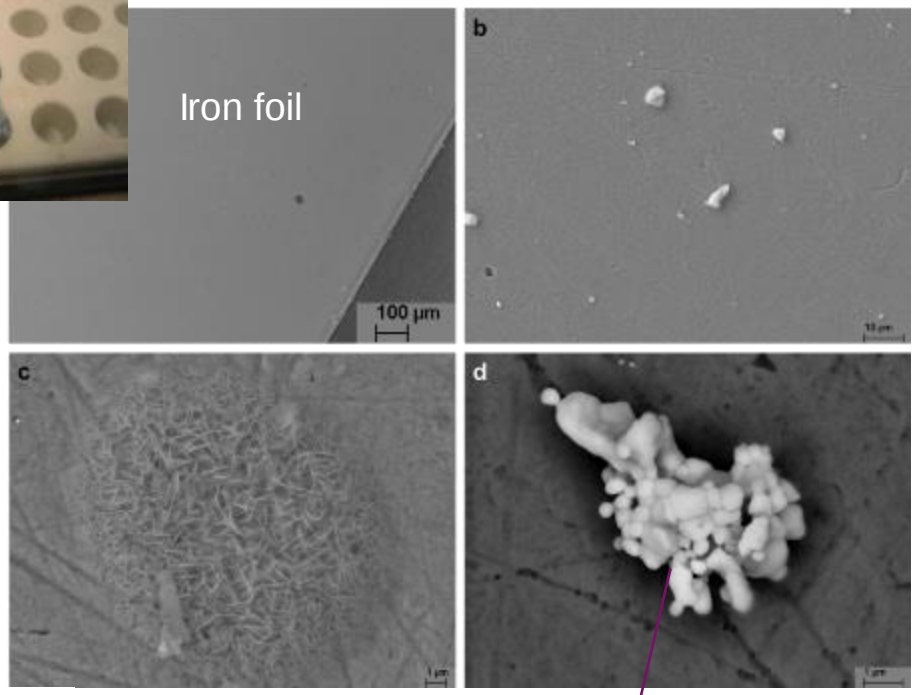
H1: oxidative dissolution and subsequent reduction / precipitation of uranium ?

H2: inhibition of the oxidative dissolution ?

Consideration of the environment on the oxidative dissolution of MOX7.5 wt.%

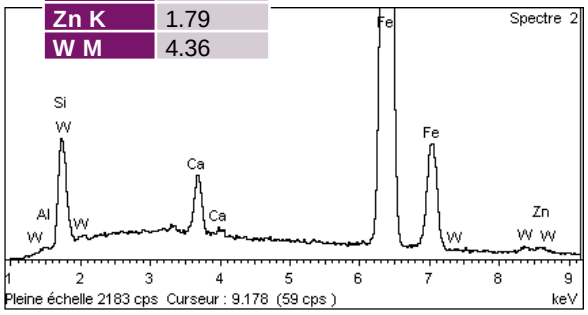
Surface characterizations (COX GW + iron foil)

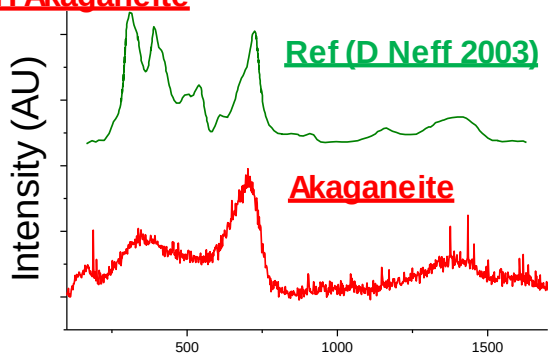


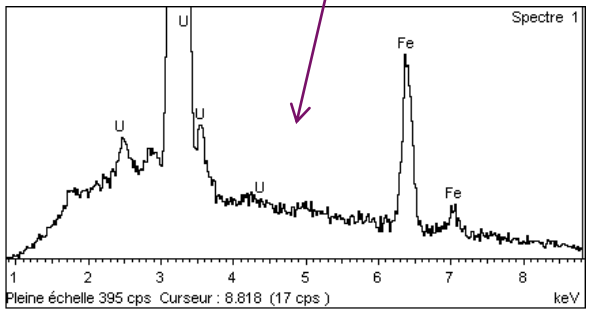


Element	Wt.%
Mg K	1.21
Al K	1.41
Si K	7.52
Cl K	0.97
Ca K	1.82
Fe K	80.92
Zn K	1.79
W M	4.36

A massive precipitation of iron (Fe(III)) hydroxide
β FeOOH Akaganeite



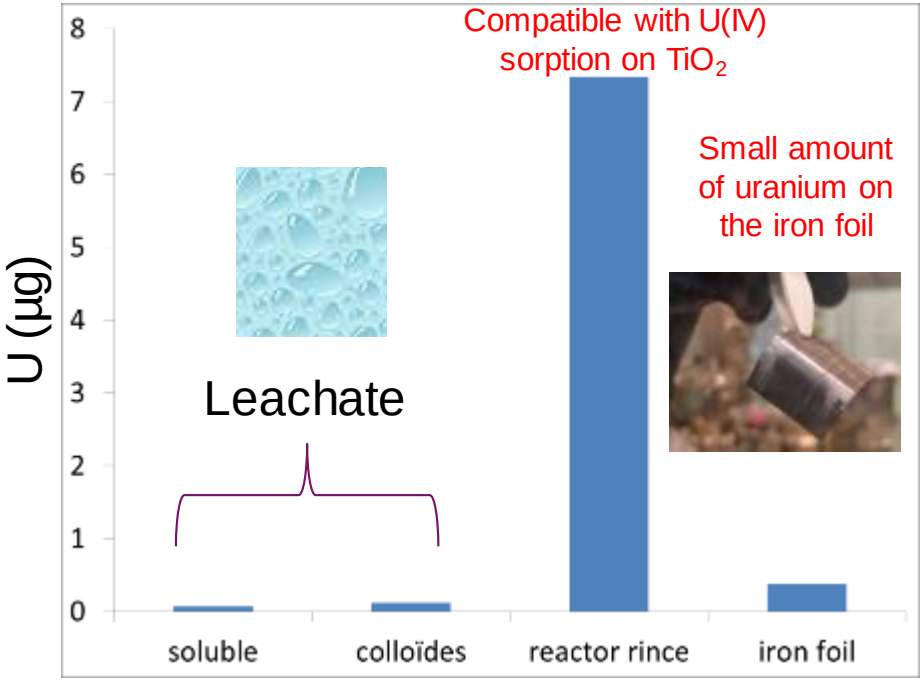


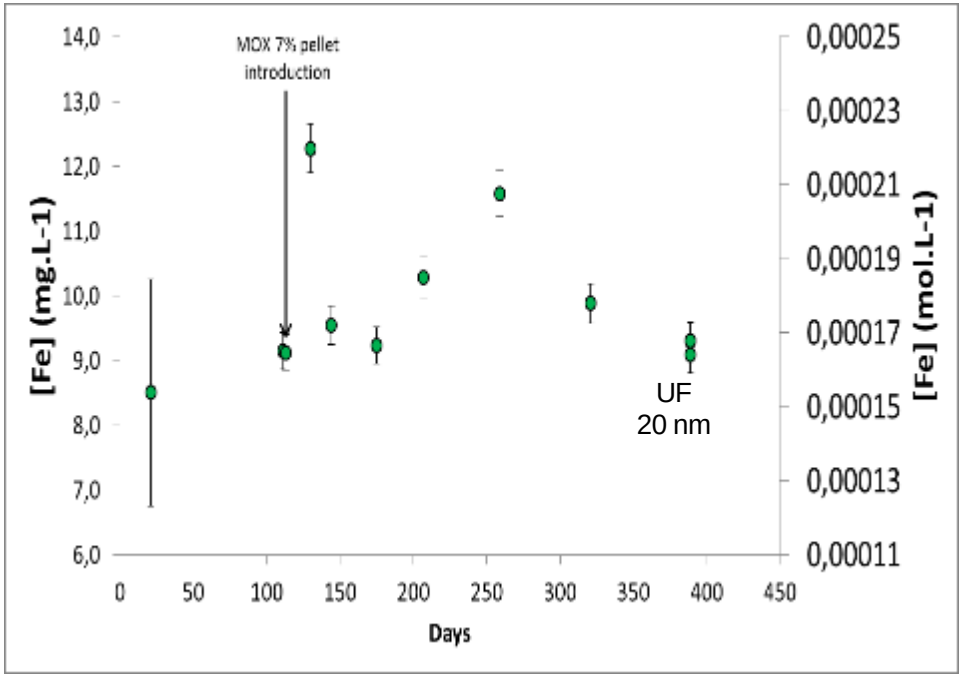


Consideration of the environment on the oxidative dissolution of MOX7.5 wt.%

Mass balances into the solution (COX GW + iron foil)

<1.3 U(IV).nm^{-2}
Latta et coll. 2014 Environmental Science and Technology





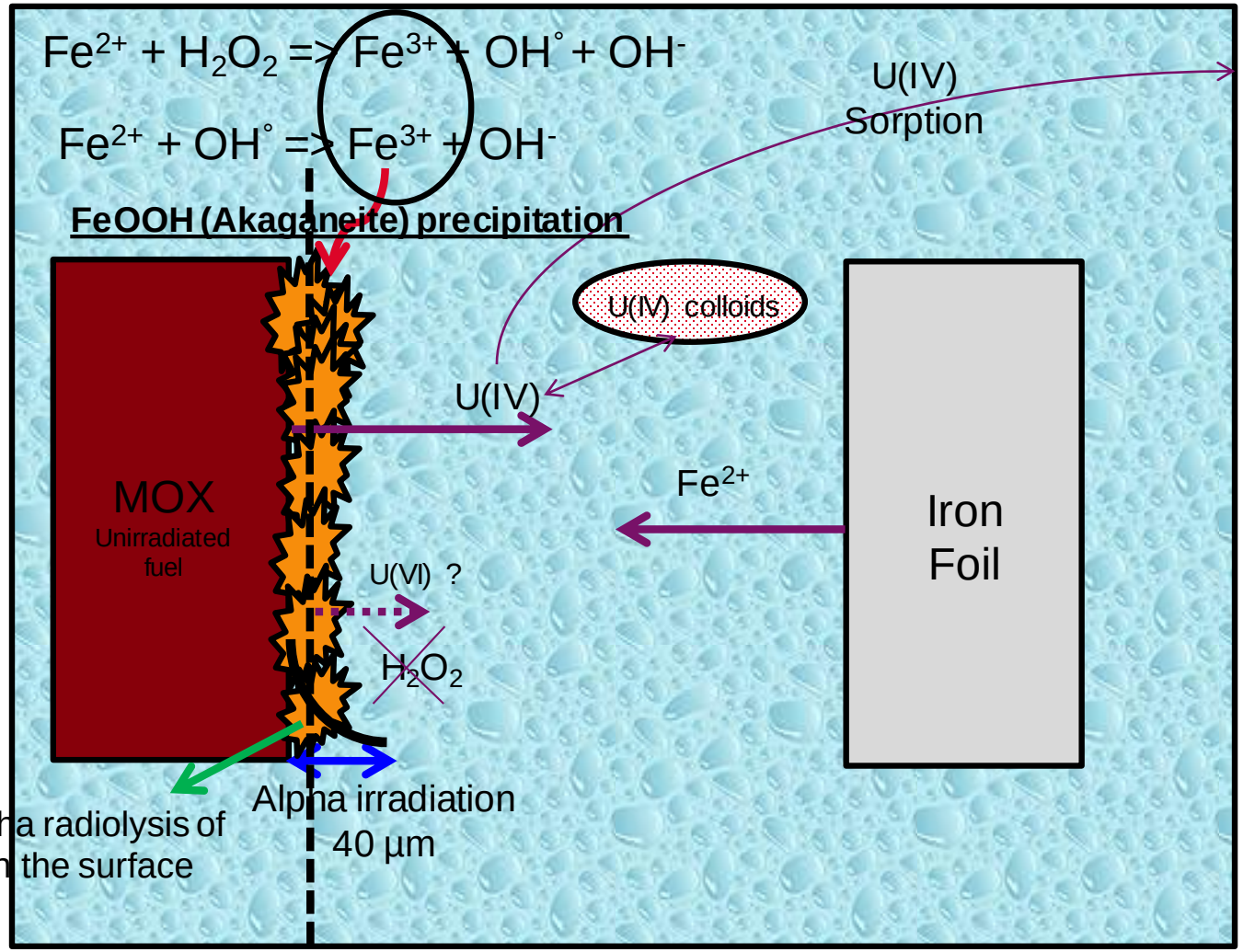
In the presence of iron the total amount of dissolved uranium is only 8 µg !

In the presence of iron, the solution was clear and no significant amounts of colloids were detected

A significant oxidative dissolution followed by a reduction of uranium into the homogeneous solution or at the iron foil surface is not observed

Mechanistic Scheme for the Mimas MOX (7.5 wt.%) fuel dissolution under alpha irradiation in the presence of iron

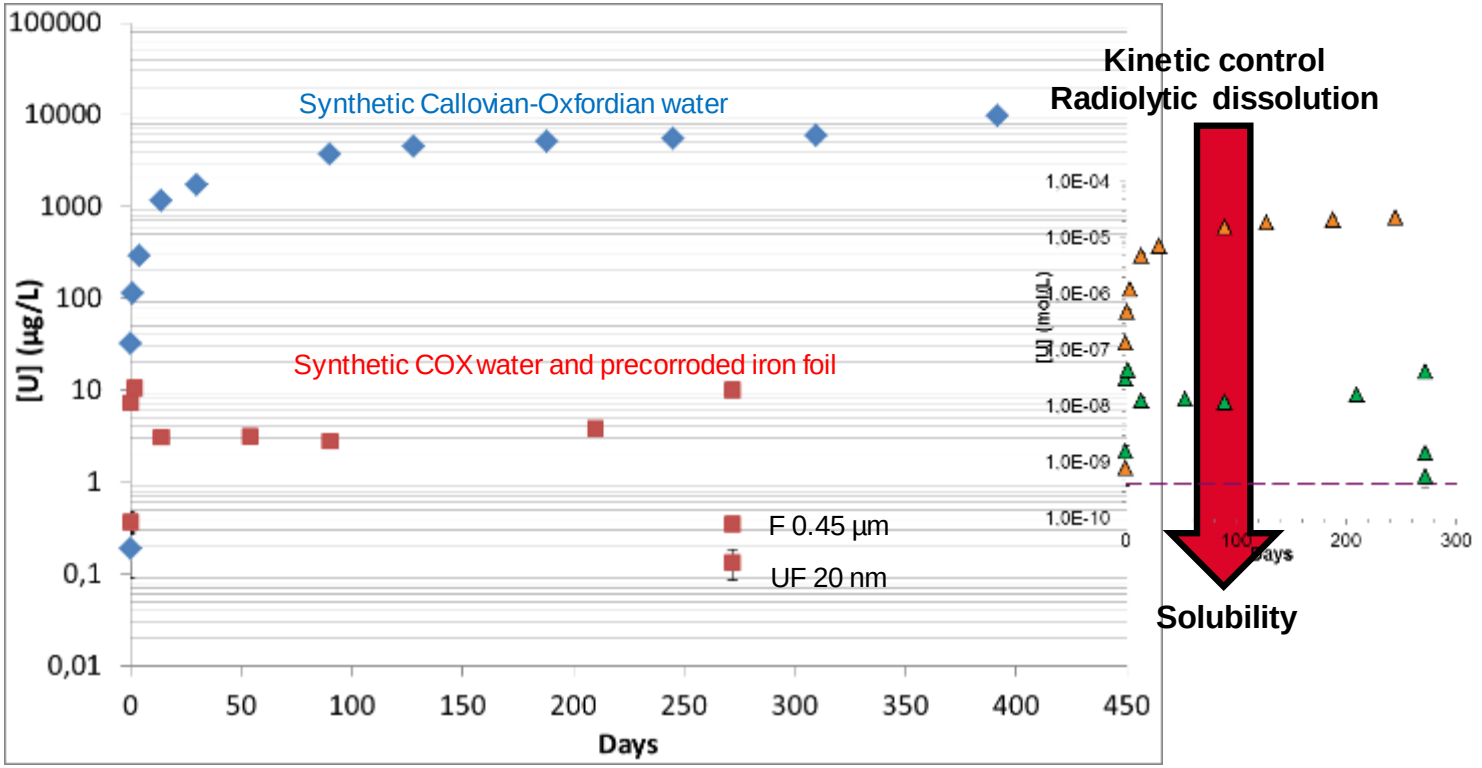
The Redox front is closed to the surface under alpha irradiation



What about irradiated MOX47 fuel ?

Preleached SF fragments in carbonated water

Uranium concentrations



To what extent the presence of iron inhibits the oxidative dissolution ?

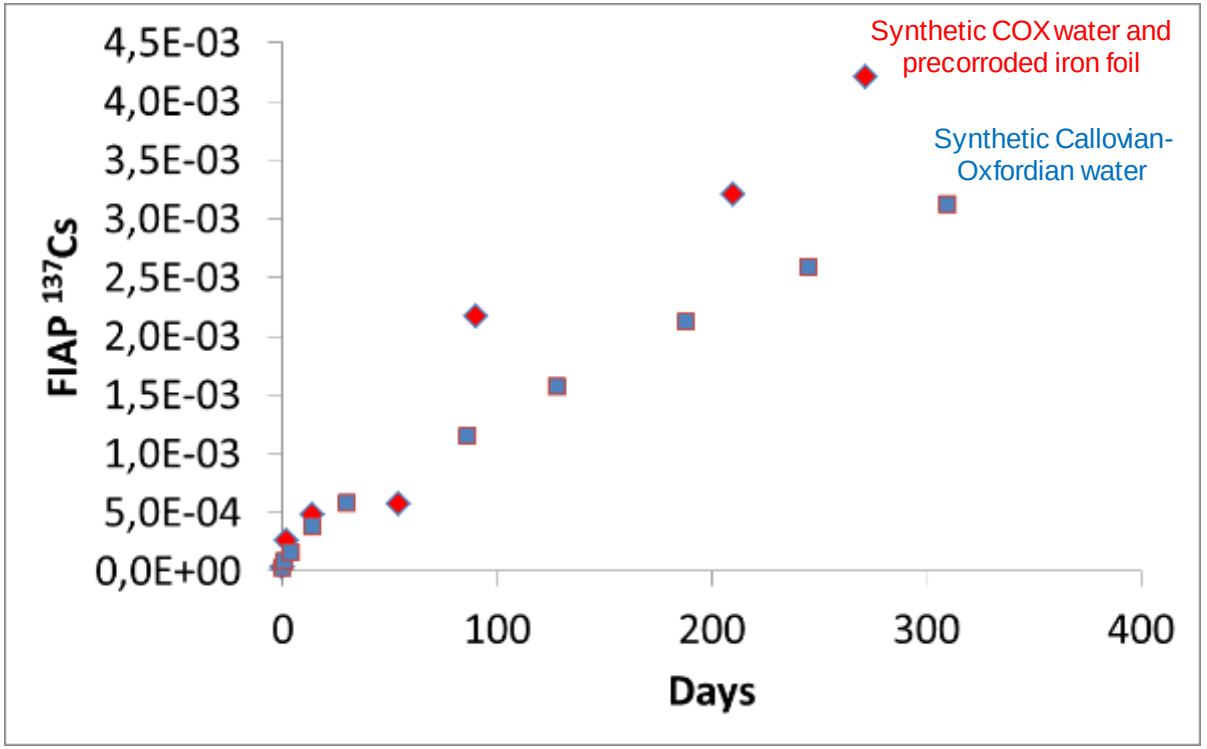
H1: oxidative dissolution and subsequent reduction / precipitation of uranium ?

H2: inhibition of the oxidative dissolution ?

What about irradiated MOX47 fuel ?

The spent fuel fragments were washed to remove labile inventories

The release of non redox-sensitive fission products ($^{134/137}$Cs and ^{90}Sr) is assumed to be controlled by the dissolution of the fluorite matrix



Is it a questioning of the previous conclusions ?

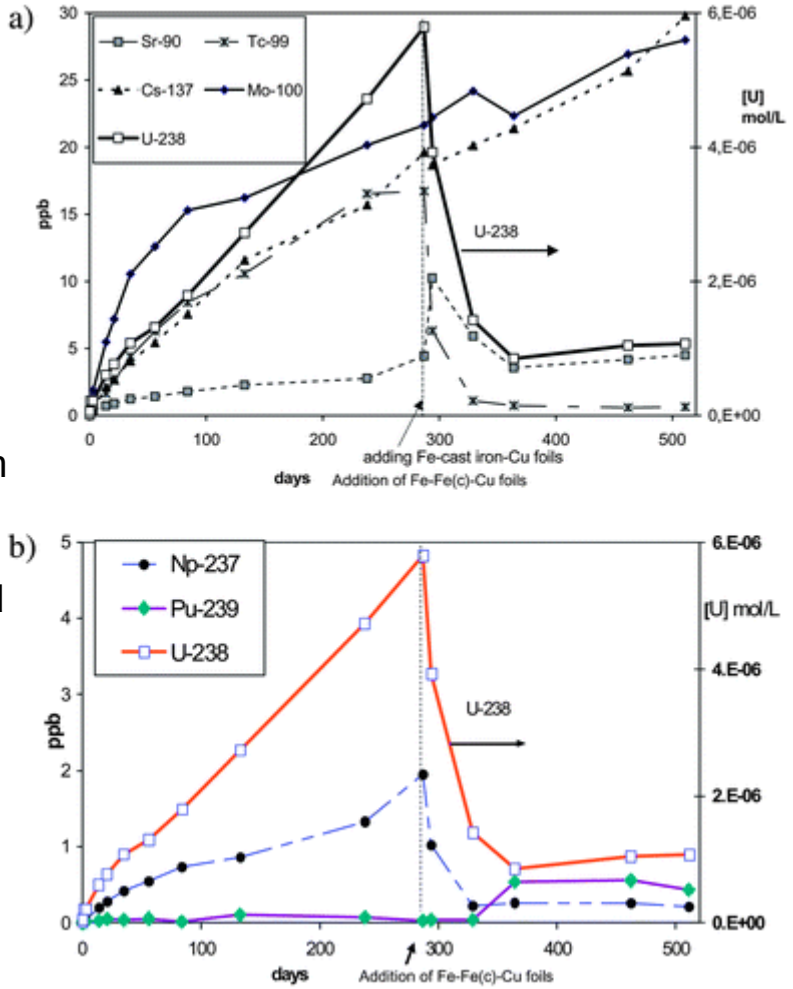
The dissolution of SF continued even though the concentrations of uranium dropped in the presence of iron

What we learn from the literature on UOX fuels…

UOX47

Daqing Cui et coll. Energy and Environmental Science (2011)

« It should be mentioned that the dissolution of SNF continued even though the concentrations of some redox-sensitive radionuclides dropped due to the insertion of metallic iron. »



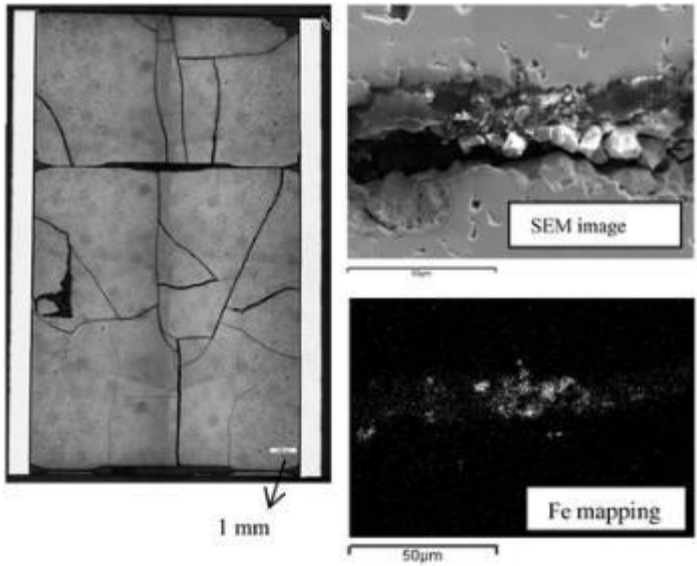
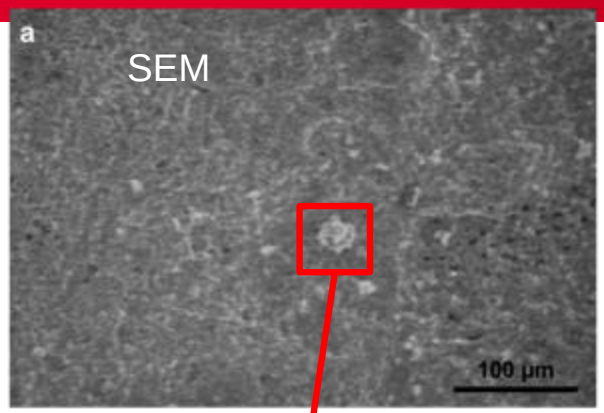
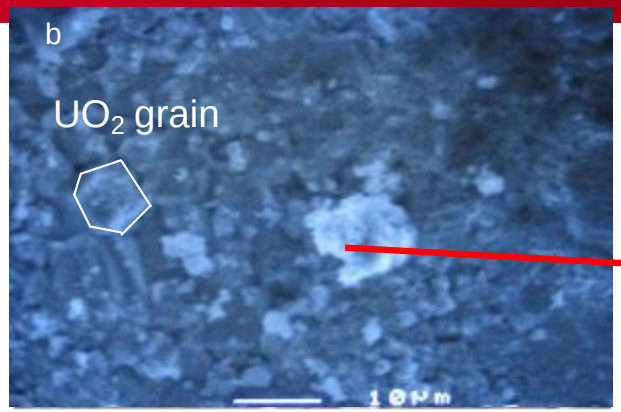


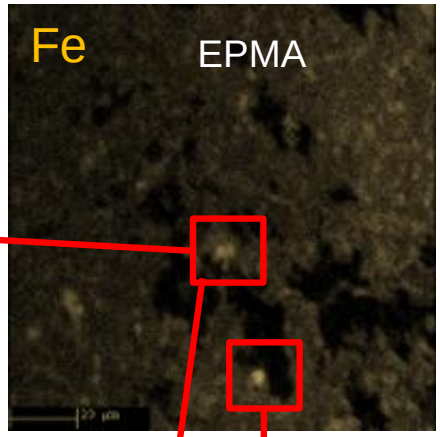
Image of the cross-section of the SNF segment (1.5 fuel pellet) that has interacted in FeCO3 saturated solution. SEM image-EDS Fe mapping shows iron oxide precipitate in the cracks.

Consideration of the environment on the oxidative dissolution of MOX47

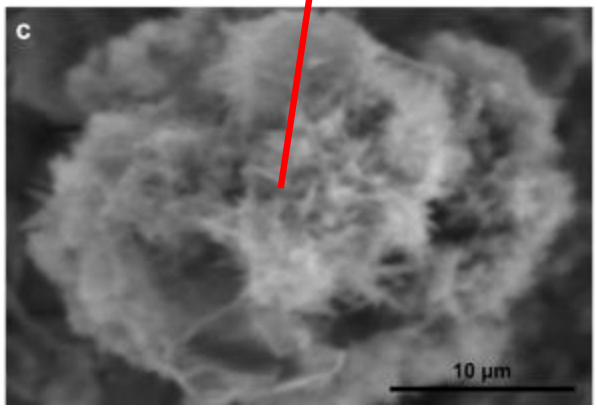
Spent fuel fragments characterizations (SF + COX GW + iron foil)

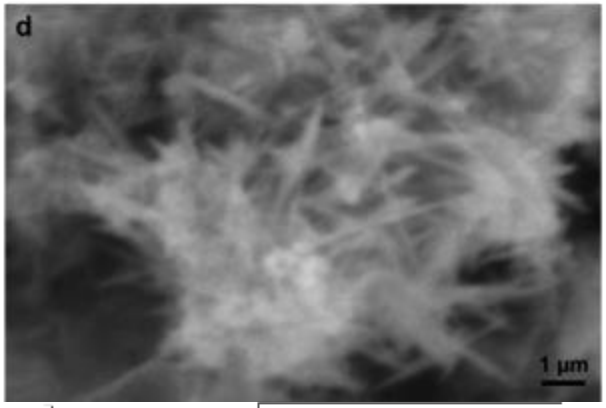


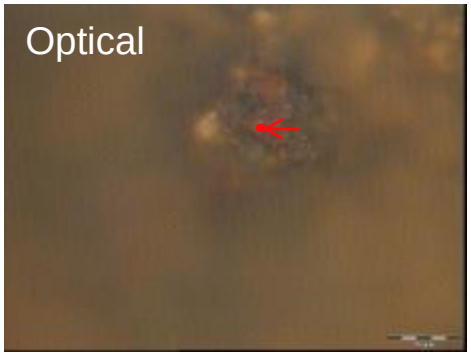


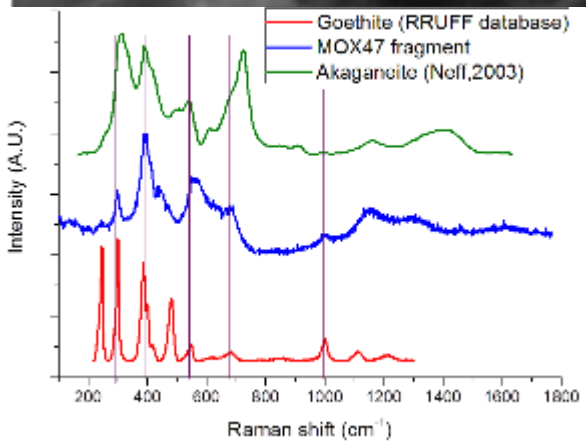


Presence of iron enriched spots







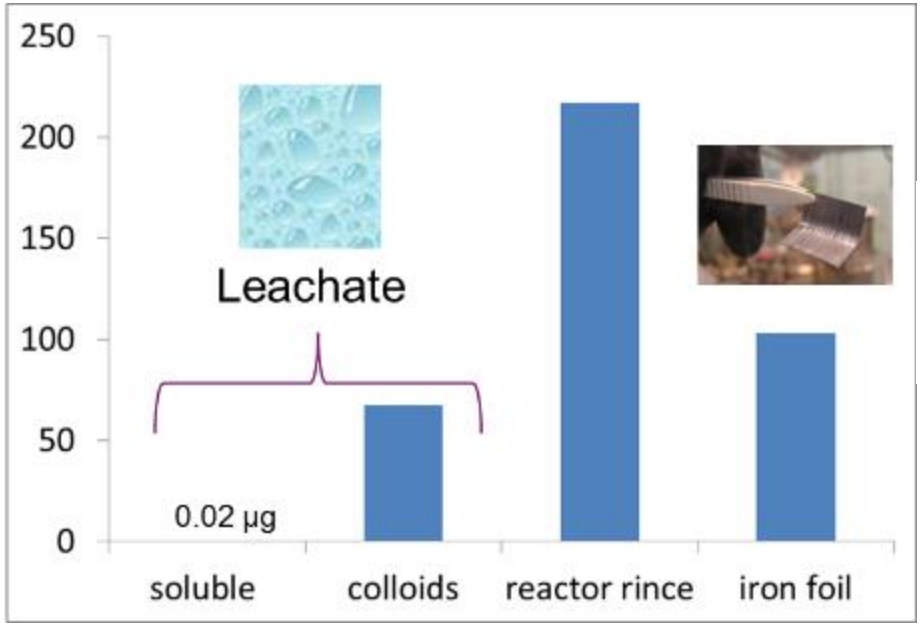


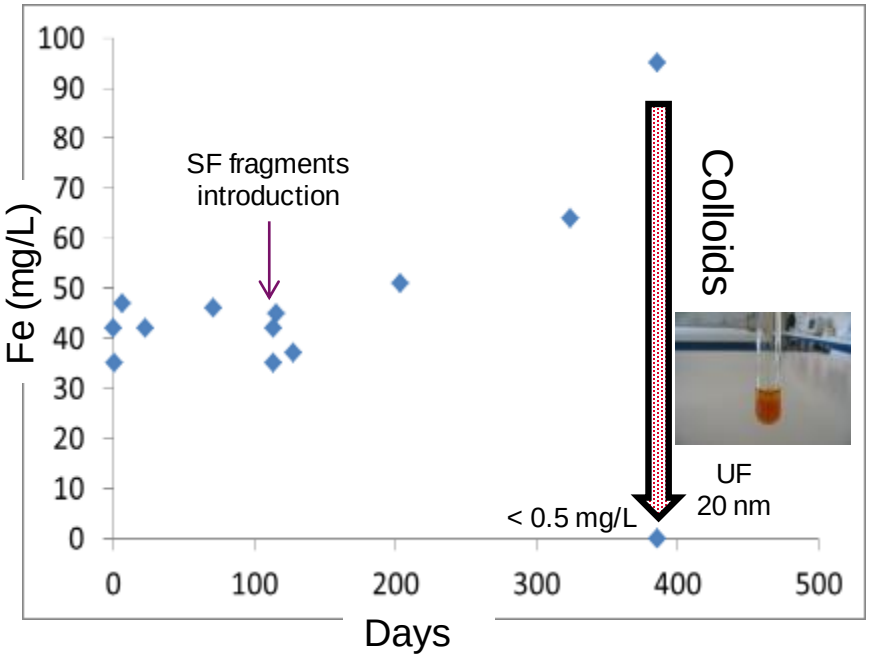
Iron precipitated on the surface of the spent fuel fragment but **very sparsely**

FeOOH precipitation

Consideration of the environment on the oxidative dissolution of MOX47

Mass balances into the solution (SF + COX GW + iron foil)





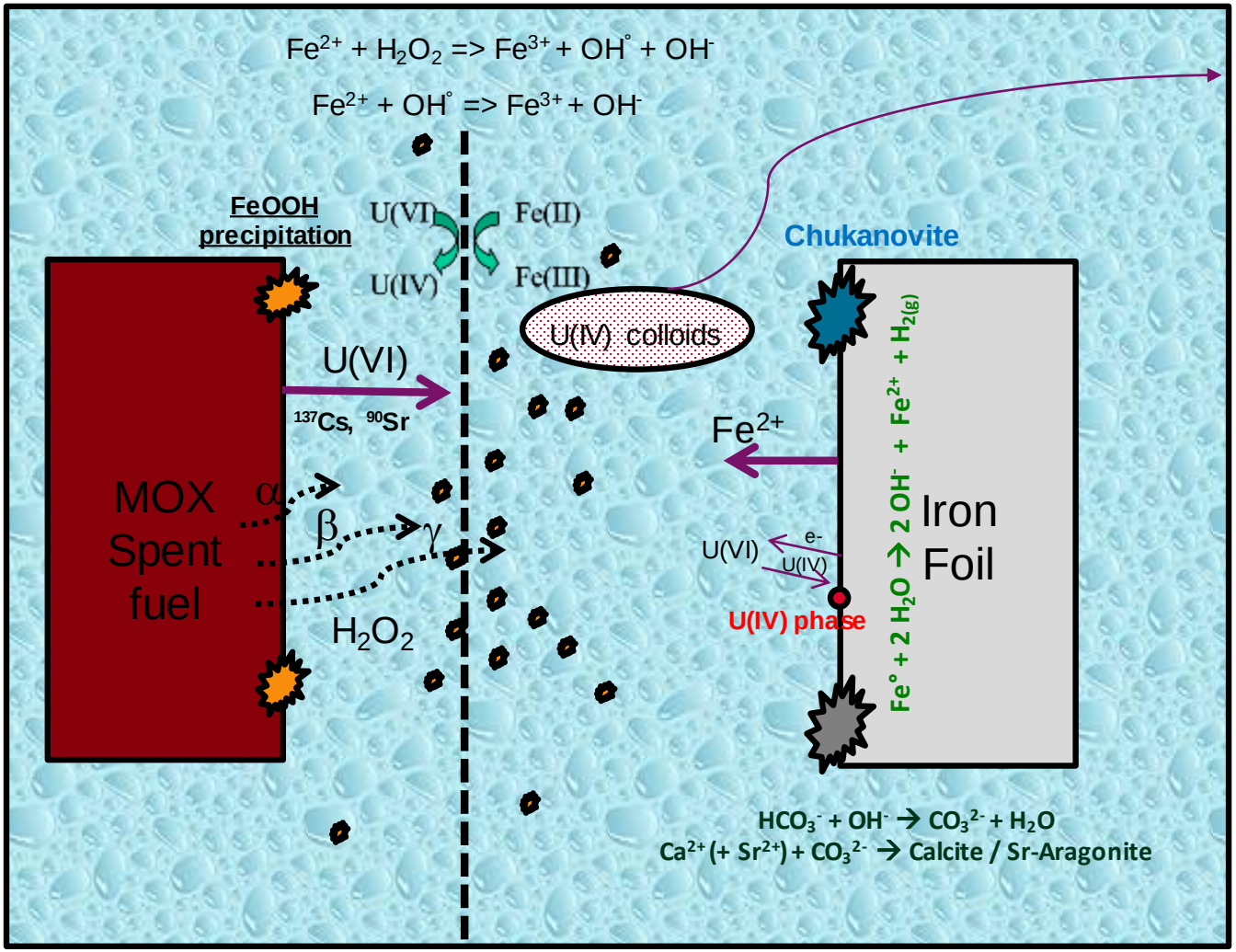
In the presence of iron a significant amount of dissolved uranium is found ≈ 400 µg

In the presence of iron, the solution was brown and no iron was detected after filtration (0.45 µm) and U-Filtration

An oxidative dissolution is confirmed for the MOX spent fuel and a massive precipitation of iron takes place into the solution

Mechanistic Scheme for the Mimas MOX47 fuel dissolution under αβγ irradiation in the presence of iron

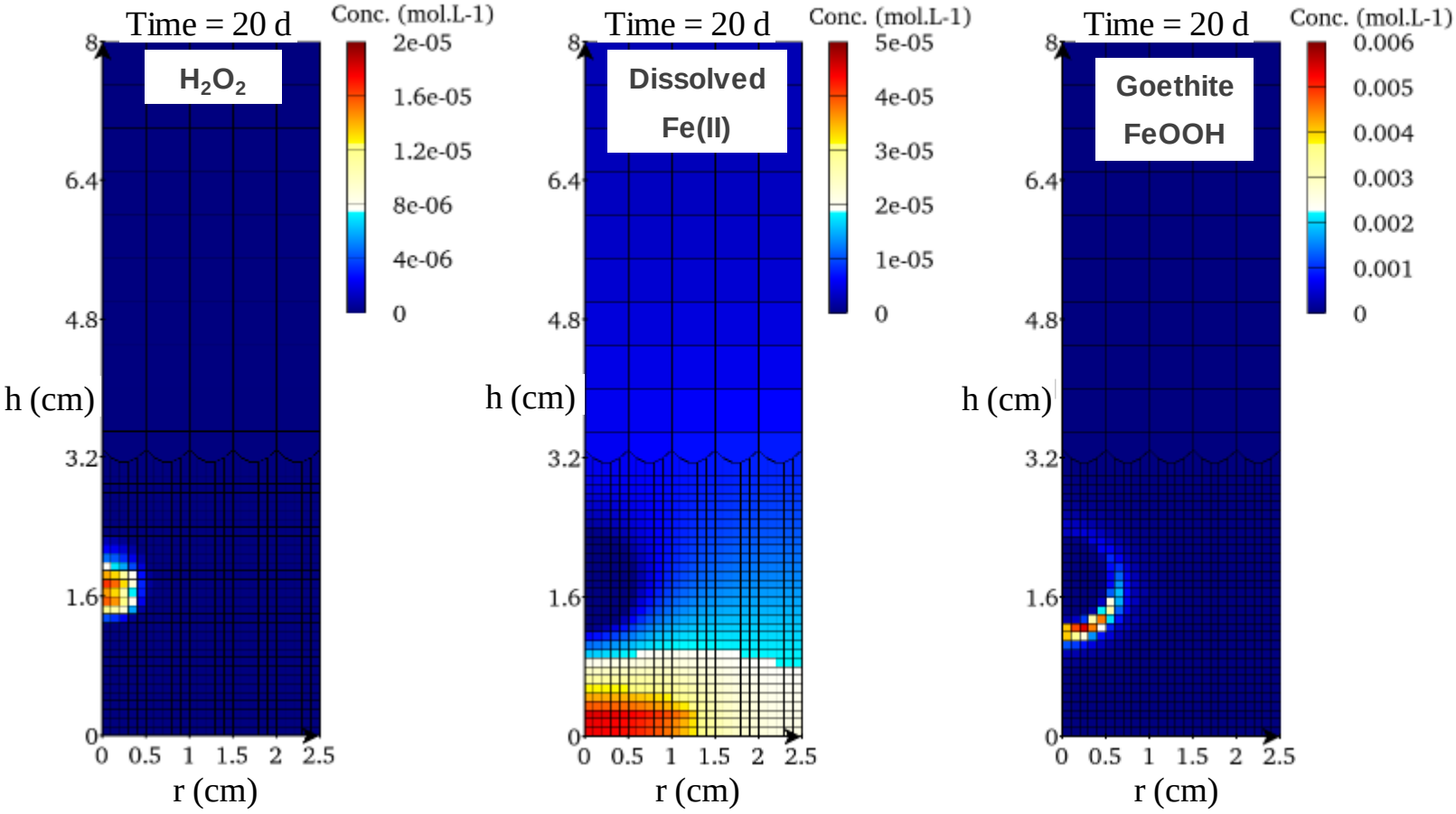
The redox front is located farther from the surface for spent fuel



Redox front

Modeling of lab test

Displacement of the redox front



If H_2O_2 primary production is increased by 50

→ the precipitation front of FeOOH is shifted in solution

CONCLUSIONS ON MOX FUELS

In first approach there is a strong similarity in behavior between UOX and Mimas MOX fuels

Mechanisms are similar both in simple systems and under environmental conditions

⇒ Oxidative dissolution under alpha radiolysis
⇒ Switching from a system controlled by the oxidative dissolution to the solubility of U(IV) in the presence of electroactive species (iron + hydrogen)
⇒ Concerning the inhibition of the oxidative dissolution the redox front location is a key issue (pay attention to the methodology of studies (irradiation fields) that plays on this location)
⇒ Difficulties are encountered in defining matrix alteration tracer under reducing conditions

Nevertheless there are some specificities associated to the Mimas MOX Fuel / UOX fuel

=> high heterogeneity in terms of reactivity and microstructure but the plutonium enriched aggregates are stabilized and more resistant to the oxidative dissolution despite a more intense irradiation field
=> higher alpha activity (= higher U dissolution) for the same burnup and the same alpha decay duration

Outlooks

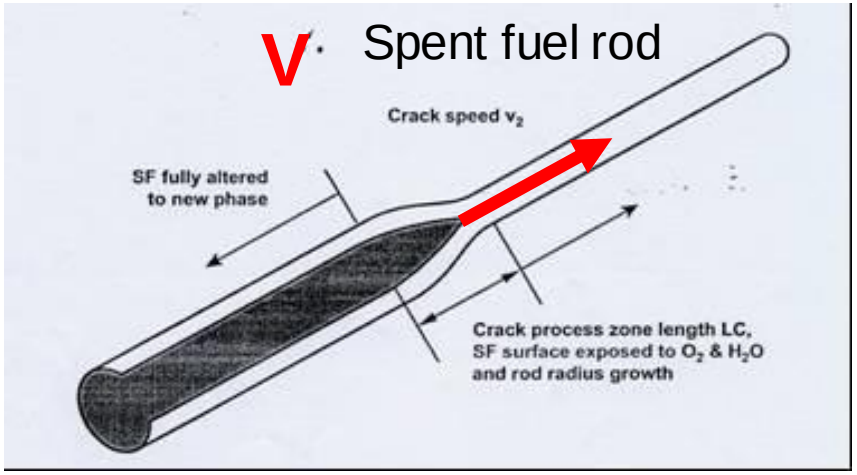
A scientific modeling incorporating these features is ongoing associated with dedicated experiments (pure solid solutions with different plutonium contents, dedicated methodology is developed on spent fuel to quantify the origin of the fission products releases…)

OUTLINES

- Introduction
- Spent Fuel Corrosion processes under geological disposal
  - Radionuclides source terms
  - Spent fuel matrix alteration mechanisms : UOX fuel case
  - Spent fuel matrix alteration mechanisms : MOX fuel case
- Spent Fuel Corrosion processes under long term interim storage
- Conclusion

Long-term interim storage of MOX spent fuel assemblies in pools

Incidental scenario: presence of an undetected defect or weakness point on the cladding which may progress over time



Crack process zone where the crack propagation is driven by alteration and expansion of the spent fuel solid

Radiolytic oxidation of the matrix together with the formation of secondary phases subject to volume expansion could then no longer be disregarded, and **could enhance the degradation of the failed rod**

O'Connell W. Clad Degradation-Wet Unzipping, Attachment III. Report ANL-EBS-MD-000014 REV00. Office of civilian radioactive waste management.

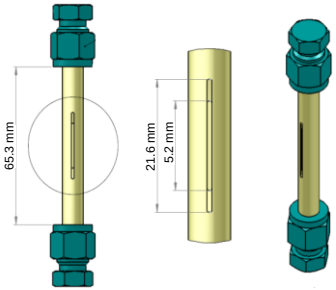
$$V = \pi\,[\mu/\sigma_{yield}]\,D\,R$$

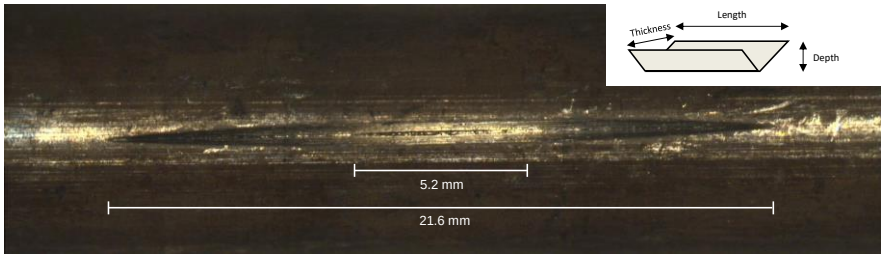
What is the nature of the secondary phases formed and the volume expansion factor (**D**)?

What are the MOX spent fuel leaching mechanisms ?
What are the dissolution rates under interim storage conditions (**R**)?

AIMS AND EXPERIMENTAL APPROACH

- Carrying out a **defect** (crack-type) on a MOX spent fuel segment (47GWd/t) leading to the water exposure of the SF matrix

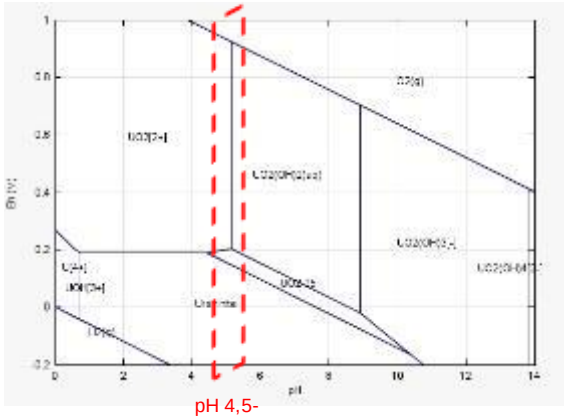




- Leaching test under wet interim storage conditions

Aerated pure water and slightly acidic conditions (pH 5)

Under γ external irradiation (210 Gy/h – 30 to 40 years of $\beta\gamma$ decay) = strong oxidizing conditions



pH 4,5-5.5

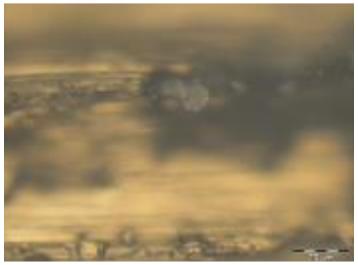
Evolution of the defect size = dimensional monitoring

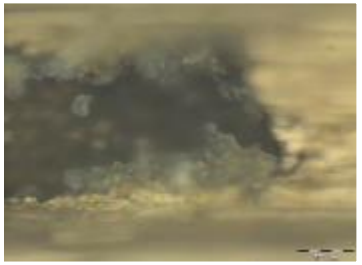
Solution analysis and radiochemistry

Identification of the secondary phases precipitating on the surface

SURFACE STATE OF THE DEFECT EXTREMITIES

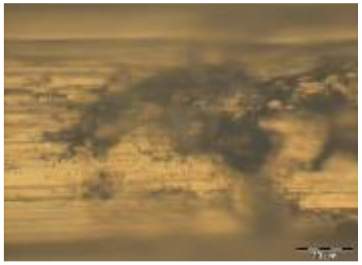
Initial observation





After 497 days of leaching

First observation of precipitate phase
Recovery of the almost all spent fuel matrix



After 750 days of leaching

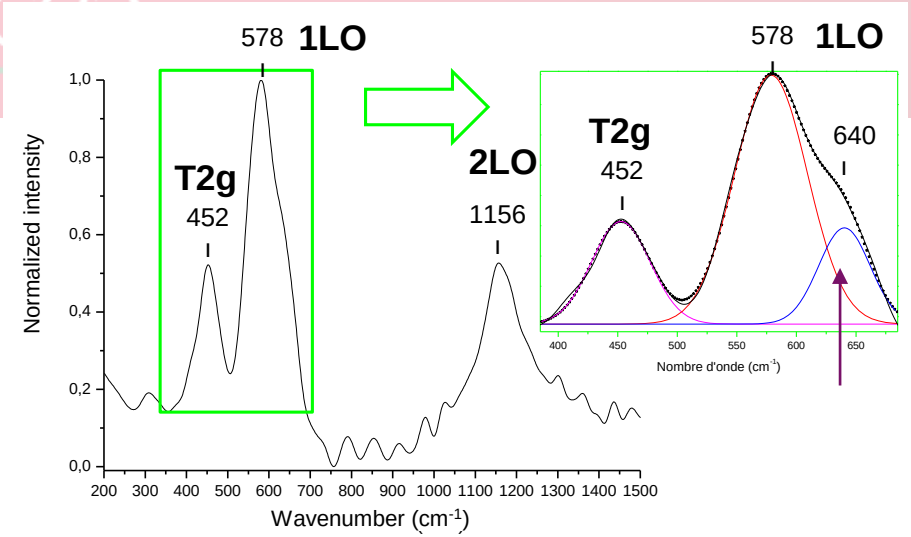
Damaging of the ZrO_2 layer

Today after 1042 days of leaching

Precipitate phase
Recovery of the almost all spent fuel matrix

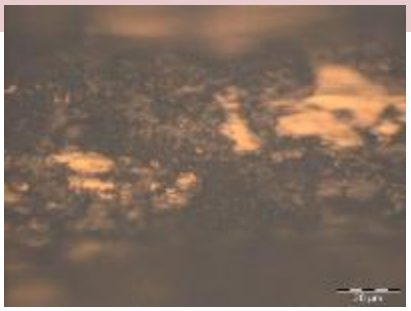
No evolution of the defect extremities

SPENT FUEL MATRIX CHARACTERIZATION (RAMAN SPECTROSCOPY)



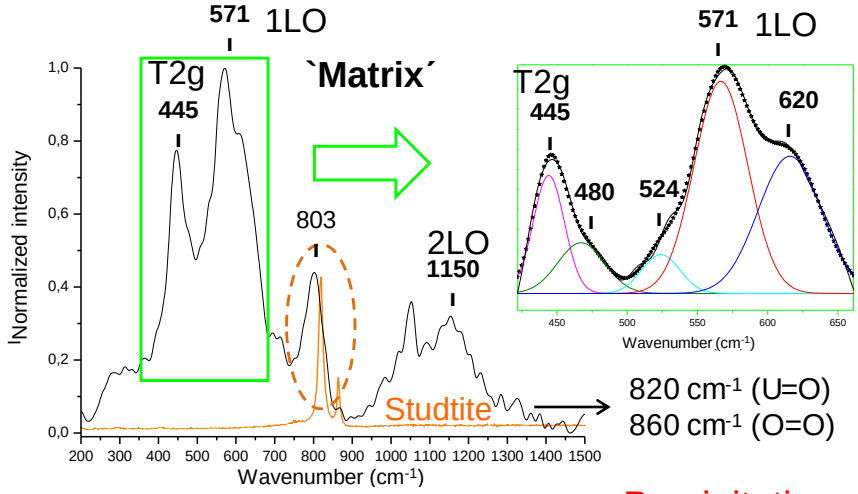
Initial characterization

Matrix spent fuel spectra:
fluorite structure of $(U,Pu)O_2$
T2g (U=O, Pu=O)
1LO
2LO

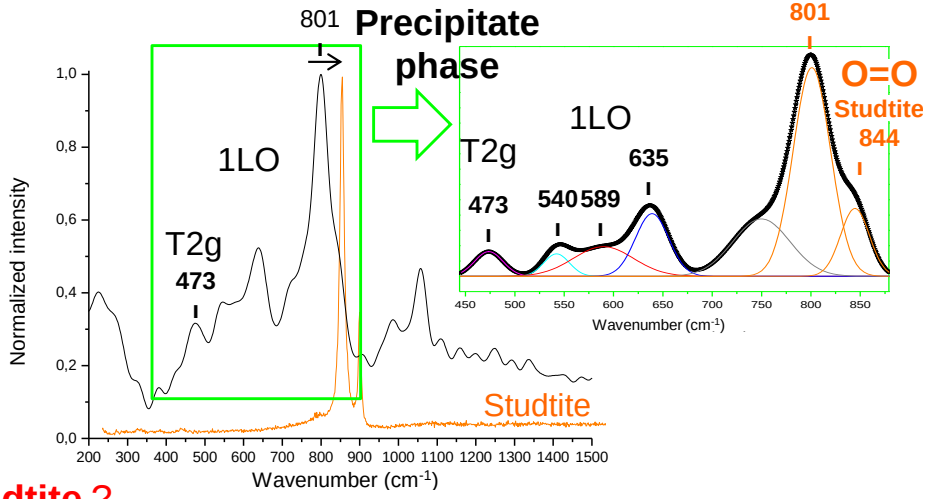


$(U,Pu)O_2$ spent fuel optical image

After 497 days



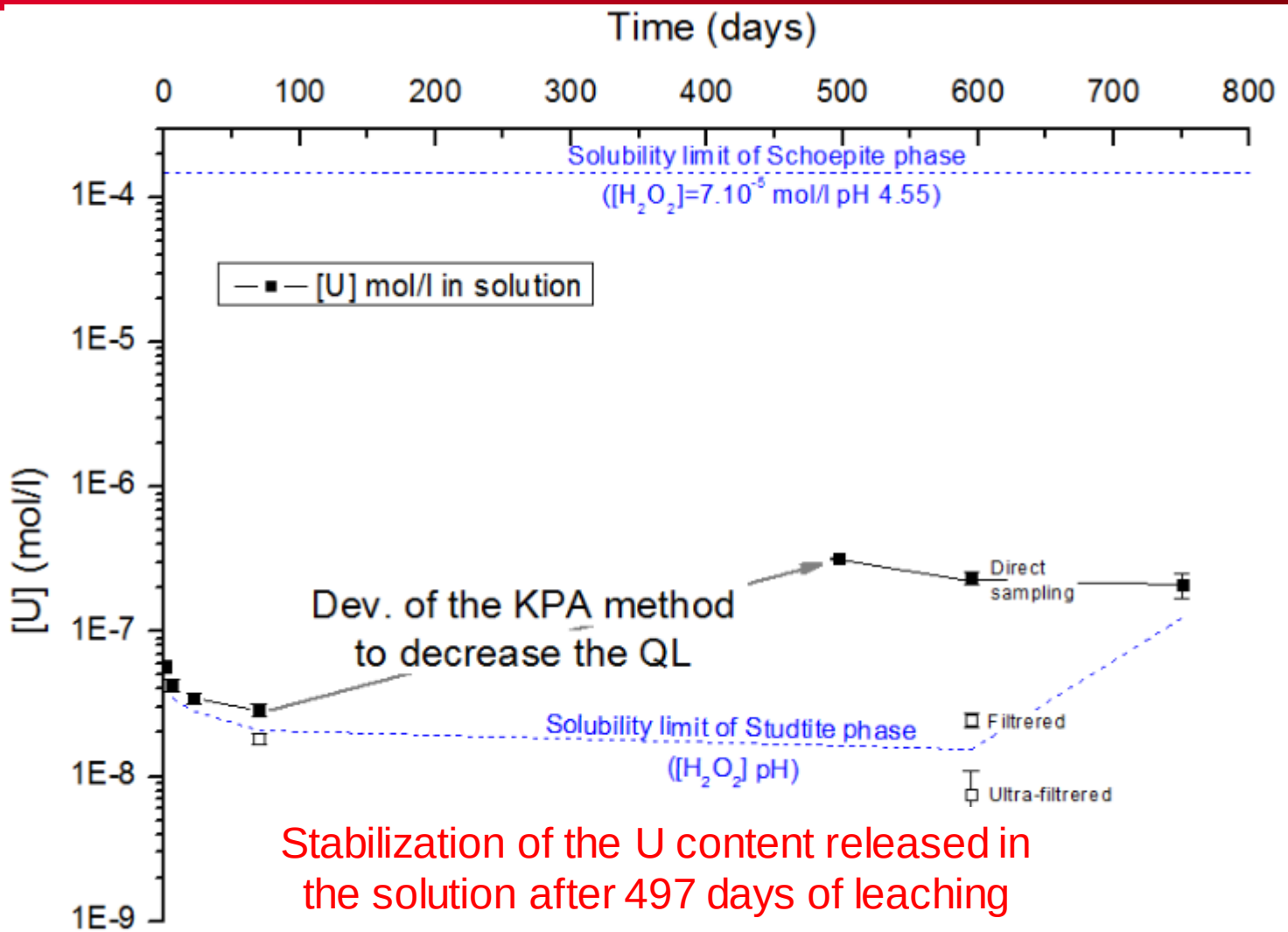
820 cm^{-1} (U=O)
860 cm^{-1} (O=O)



Precipitation of **Studtite** ?
$(UO_4.4H_2O)$

Observation most probably the **Studtite phase** (with the U_4O_9 contribution already present at the beginning)

URANIUM RELEASED IN SOLUTION



Stabilization of the U content released in the solution after 497 days of leaching

↘

U-based-secondary phase precipitation

Conclusions

Thank you for your attention

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