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Impact of ruthenium on the dissolution mechanisms of uranium dioxide



Thibault KACZMAREK

NuMat 29/10/2020

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MESBAH^a, Xavier LE GOFF^a, Nathalie REYNIER-TRONCHE^b*

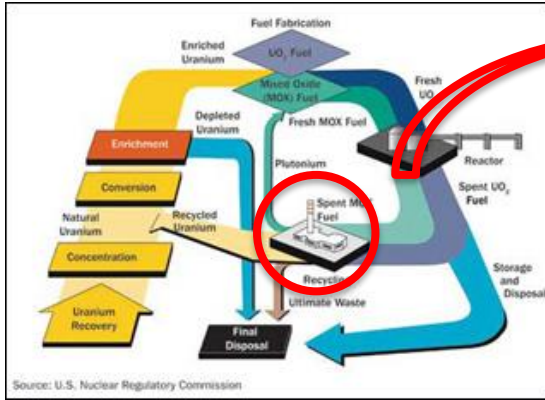
a- ICSM – UMR 5257 CNRS/CEA/UM/ENSCM, Site of Marcoule - Bât. 426, BP 17171, Bagnols/Cèze 30207, France

b- CEA/DES/ISEC/DMRC/LDCI Site of Marcoule, BP 17171, Bagnols/Cèze 30207, France

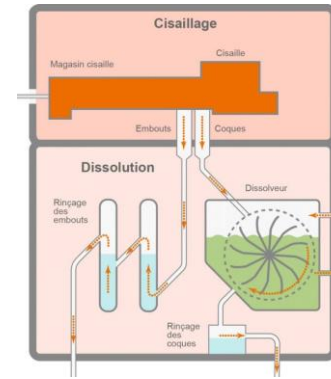
Dissolution of SNF in nitric acid solution



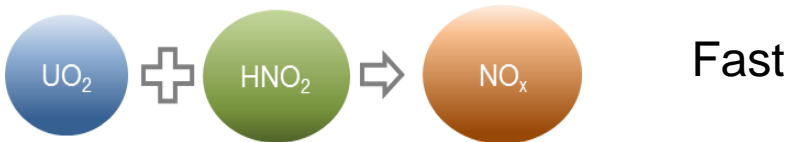
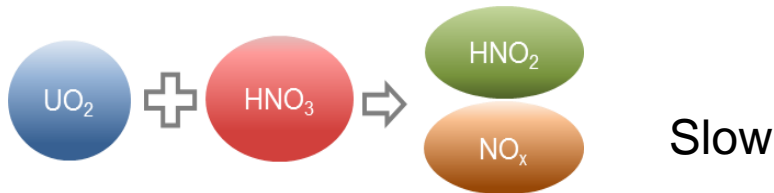
- The nuclear fuel cycle in France is a closed cycle.
- Fuel reprocessing: head-end step → dissolution.



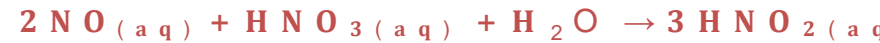
Conditions of dissolution :
3 - 4M HNO₃ ; 80 – 90 °C



Dissolution of UO₂ in a nitric medium

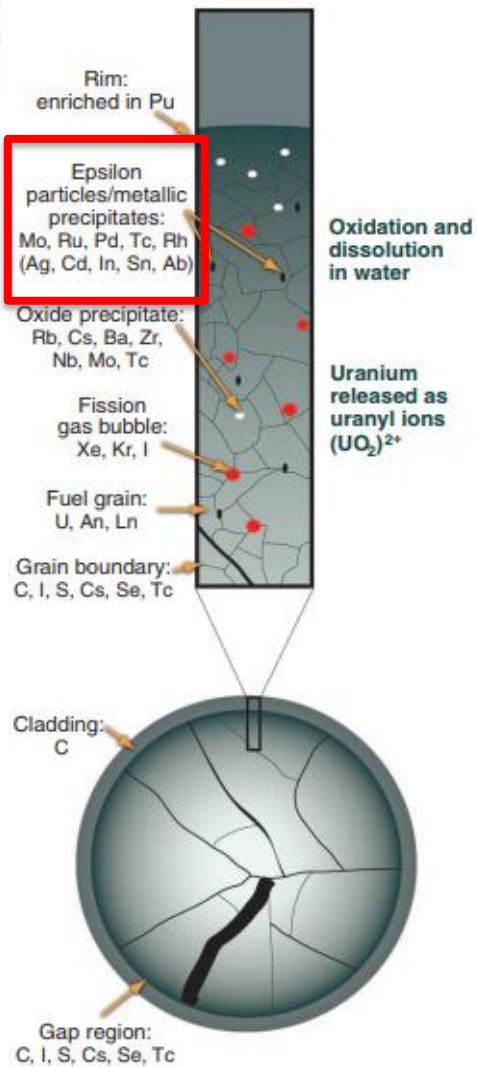


Oxidation of NO by HNO₃ to form HNO₂



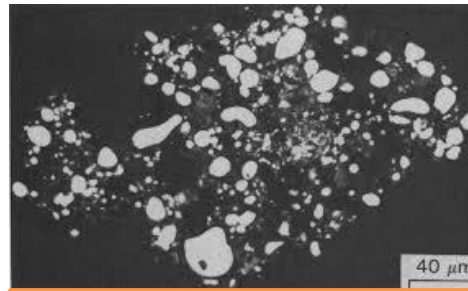
→ « autocatalytic » mechanism

Spent Nuclear Fuel



Used nuclear fuel contains 40 FPs divided into 4 families^[1].
PGM = 0.6 mol.% (52% Ru, 38% Pd, 10% Rh)

Dissolution
 HNO_3

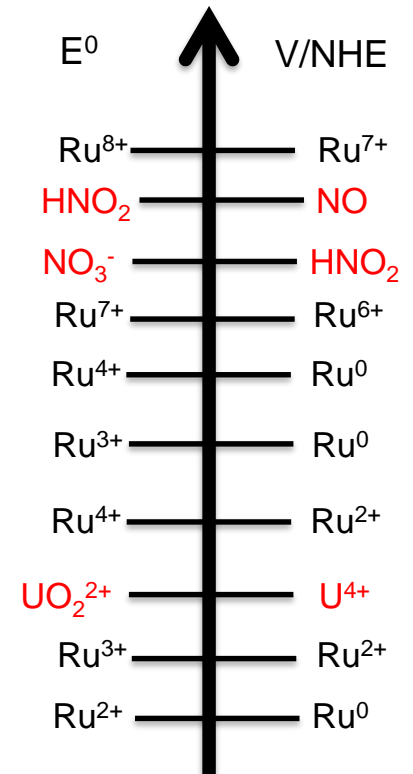


Dissolution residues ^[2]
(alloy Mo-Ru-Rh-Pd-Tc)

Main issues in the reprocessing process:

- Decrease in the effectiveness of the extractant
- Low solubility in the glassy matrix

Focus on Ru

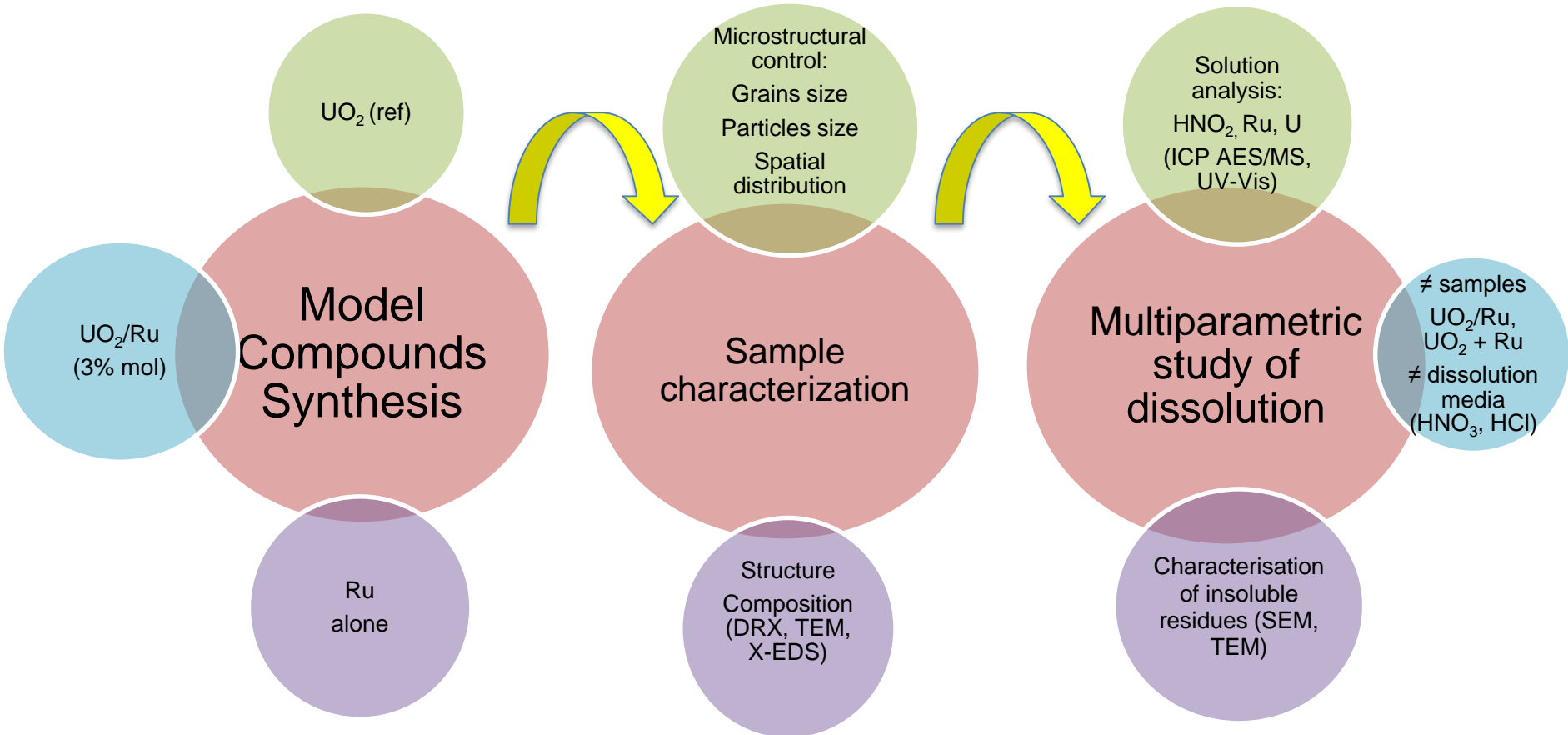


Many possible reactions between HNO_3 and Ru or between Ru and U

What impact have Ru particles on the dissolution of the fuel?

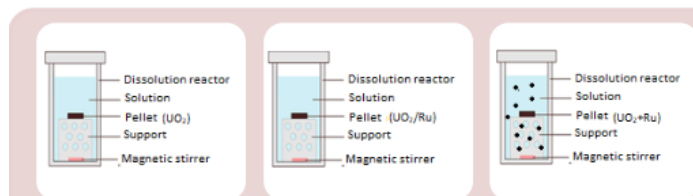
[1] P. C. Burns, R. C. Ewing, R. Navrotsky, Science, 2012, 335, 1184-1187

[2] H. Kleykamp, "The Chemical-State of Fission-Products in Oxide Fuels at Different Stages of the Nuclear-Fuel Cycle," Nucl. Technol., vol. 80, no. 3, pp. 412-422, Mar. 1988



Static dissolution:

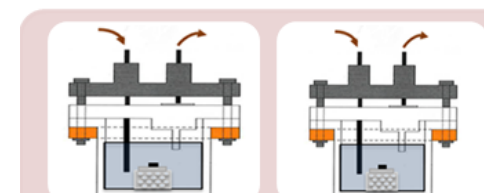
soft condition (60°C - 0.1M) with low renewal of the solution



<p>UO₂ reference</p> <p>HNO₃ 0,1M HCl 0,1M 60°C</p> <p>V= 50 ml m₀= 80,3 mg</p>	<p>UO₂/Ru (3%mol)</p> <p>HNO₃ 0,1M HCl 0,1M 60°C</p> <p>V= 50 ml m₀=105,2 mg</p>	<p>UO₂ + Ru (3%mol)</p> <p>HNO₃ 0,1M 60°C</p> <p>V= 50 ml m₀= 104,7 mg</p>
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Dynamic dissolution:

aggressive condition (80°C - 4M) with high renewal of the solution



<p>UO₂ reference</p> <p>HNO₃ 4M 80°C Q= 120 mL/h</p> <p>m₀=45,0mg</p>	<p>UO₂/Ru (3%mol)</p> <p>HNO₃ 4M 80°C Q= 120 mL/h</p> <p>m₀= 74,7 mg</p>
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Relative mass loss

$$\frac{\Delta m(i)}{m_0} = \frac{m_i}{f_i \times m_0}$$

$$= \frac{C_i(t) \times V}{f_i \times m_0}$$

Dissolution rate : $Rd(i) = \frac{d(\frac{m_i}{f_i})}{dt}$

Analysis by ICP-MS $\Rightarrow C_{Ru}$
 Analysis by ICP- AES $\Rightarrow C_U$
 Analysis by UV-Vis $\Rightarrow C_{HNO_2}$

(Griess' method)

Relative mass loss

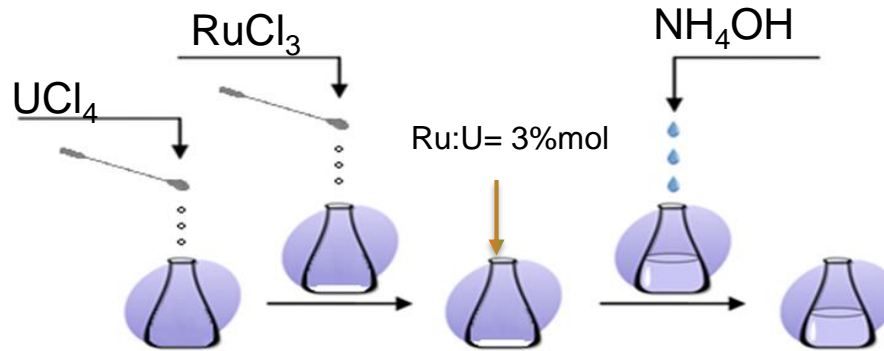
$$\frac{\Delta m(i)}{m_0} = \int_0^t \frac{C_i(t)}{f(i) \times m_0 \times Q} dt$$

Synthesis of model compounds

Synthesis of UO_2/Ru (3%mol) powder



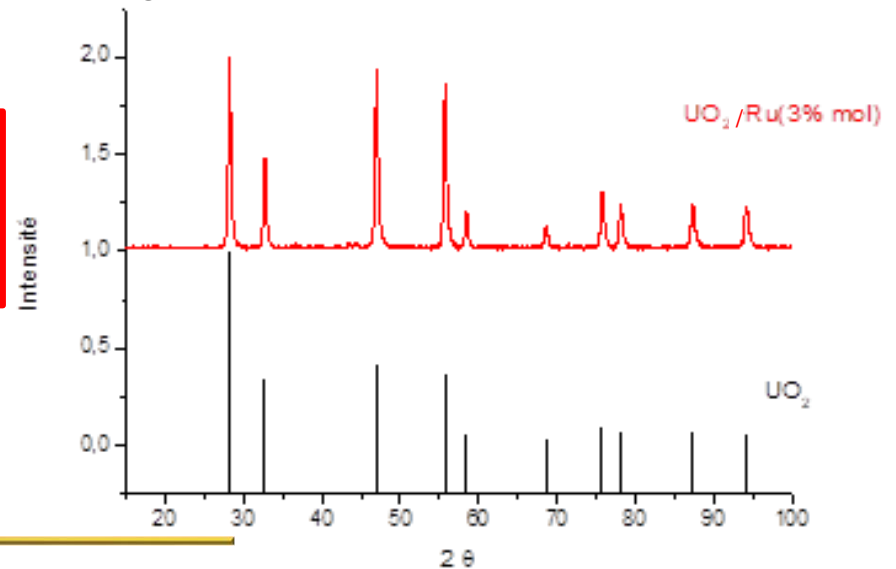
Wet synthesis: **Hydroxide route**^[3-4-5]



→ 30 min of maturation under agitation

- 2 washes with water and one with ethanol
- Recovery of the powder by evaporation of ethanol under vacuum
- Calcination in reducing atmosphere (Ar/H_2 4%) during 4h at 800°C

UO_2 : Fluorine structure ($\text{Fm}\bar{3}\text{m}$)
Cell parameter $a = 5.4643 \text{ \AA}$
Ru not detected <DL



[3] S.K Kantan, R.V Raghavan, G.S Tendolkar, 1958, 6, 132

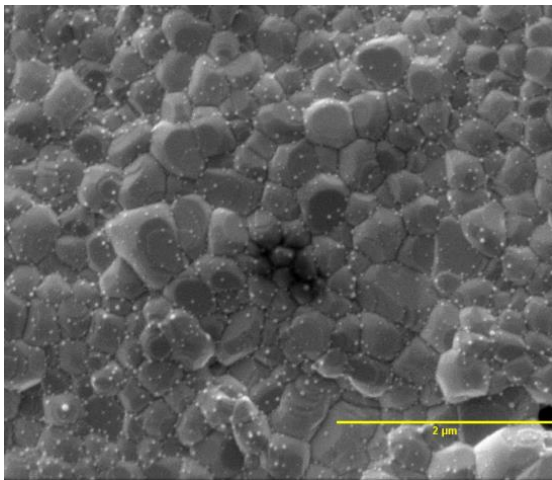
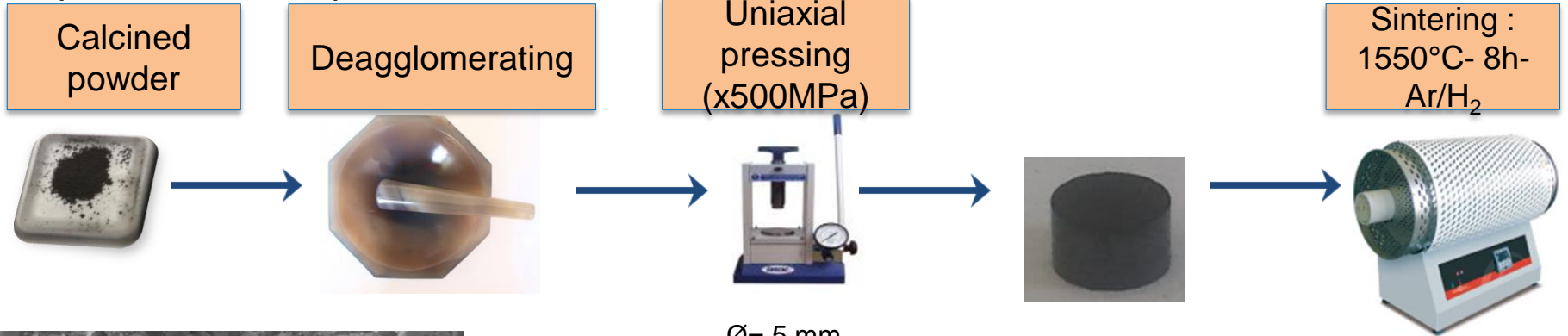
[4] D. Vivien, J. Livage, C. Mazières, 1969, 71, 199.

[5] J. Martinez, N. Clavier, A. Mesbah, F. Audubert, X. F. Le Goff, N. Vigier, N. Dacheux, *Journal of Nuclear Materials*, 2015, 462, 173-181.

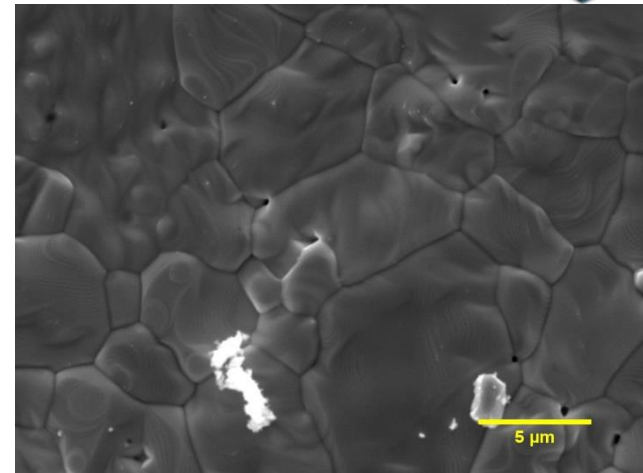
Preparation of pellets : UO_2 (ref) UO_2/Ru (3%mol)



Preparation the sample :



UO_2/Ru pellet after sintering
 $D_{\text{geo}} = 97\%$
grain size $\approx 150 \text{ nm}$



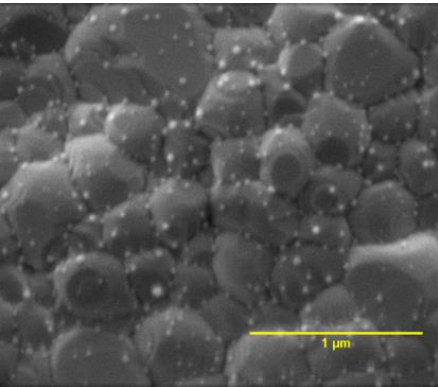
UO_2 (ref) pellet after sintering
 $D_{\text{geo}} = 95\%$
grain size $\approx 1-7 \mu\text{m}$

The presence of Ru leads to the formation of dense pellets with much small UO_2 grains.

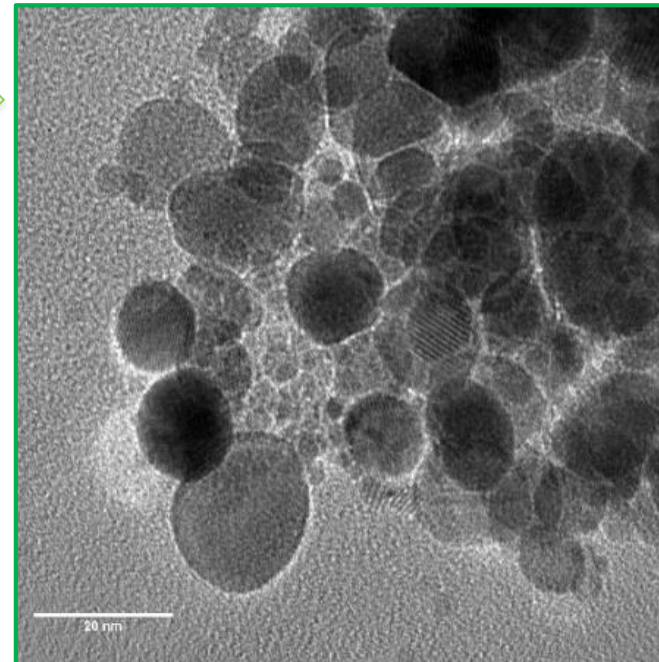
Characterizations of Ru particles in UO₂/Ru (3%mol)



Image analysis

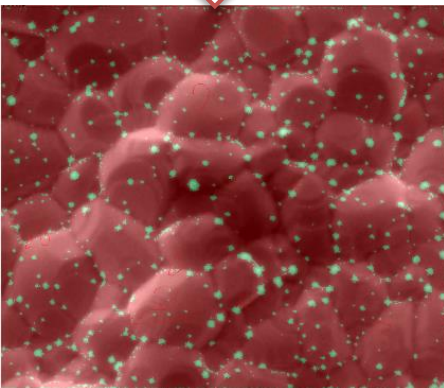


Dissolution in 0,1 M HNO₃
60°C



TEM analysis of the dissolution residues

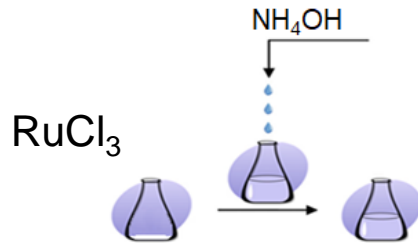
Segmentation



- Hexagonal structure(P6/3 mmc) as in SNF
- size : 1 – 15 nm (in agreement with SEM images analysis)

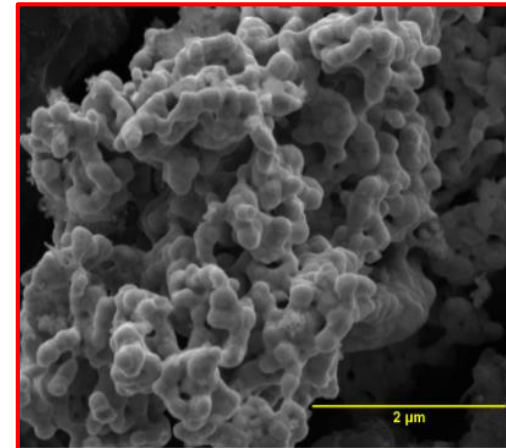
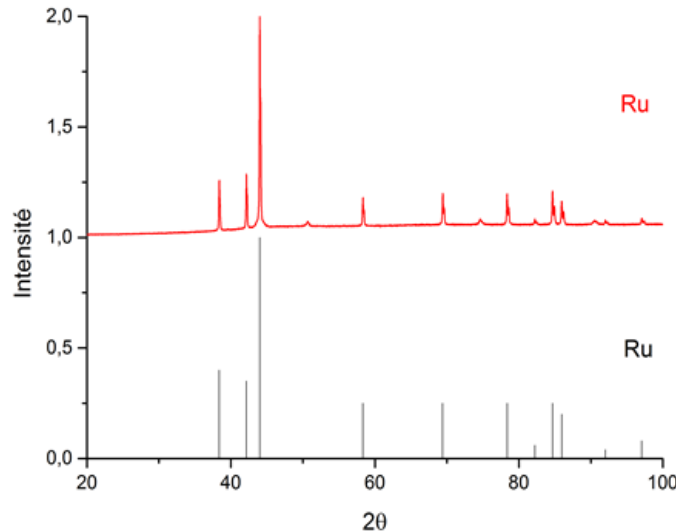
	SIZE (nm)	SURFACE COVERAGE (%)
GRAINS	144 ± 1	
PARTICLES	9 ± 1	3-4

Wet synthesis: *Hydroxide route*



→ 30 min of maturation under agitation

- 2 washes with water and one with ethanol
- Recovery of the powder by evaporation of ethanol under vacuum
- Calcination in reducing atmosphere (Ar/H_2) 4% 4h at 800°C

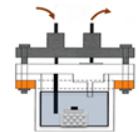


BET < DL
Low specific surface area

- Same phase as in UO_2/Ru pellets
- Size 100 to 300 nm → 10 to 30 times bigger than in UO_2/Ru
- Heat treatment → agglomerates (lower reactivity) of metallic Ru particles

Multiparametric study of dissolution

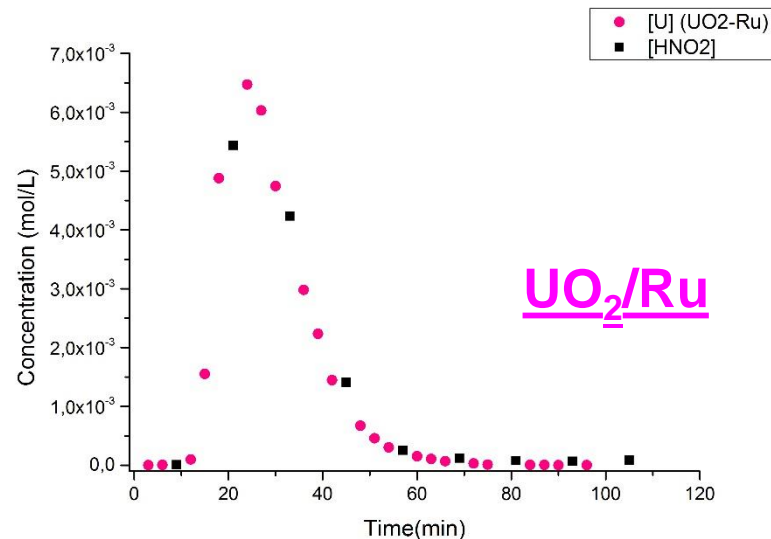
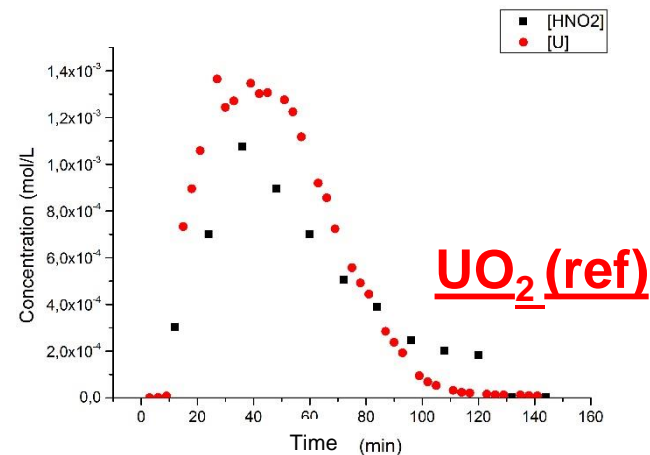
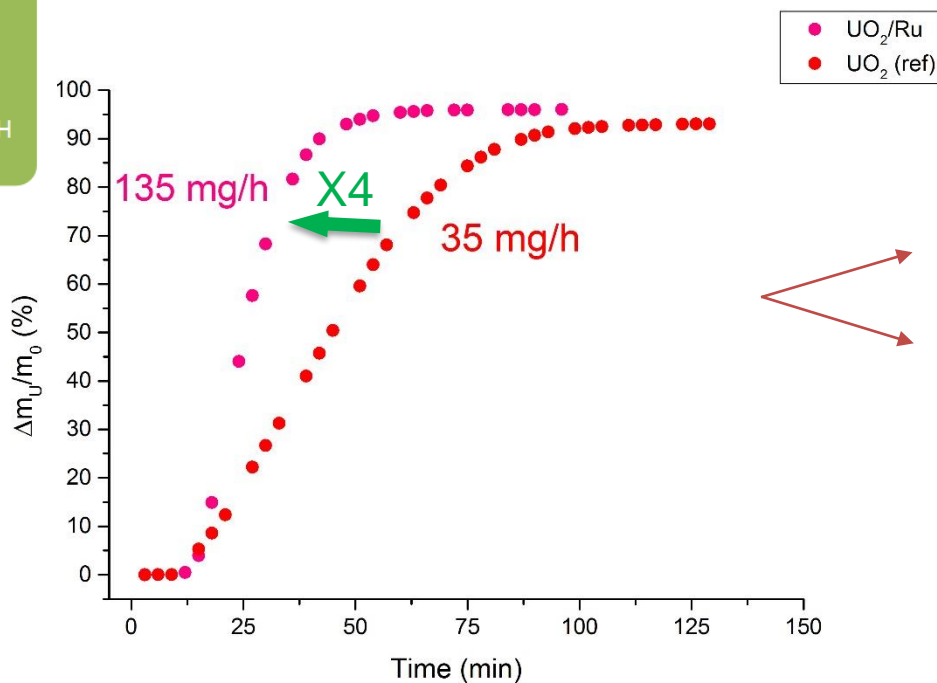
UO₂/Ru (3%mol) in 4M HNO₃ 80°C



UO₂/Ru
(3%mol)

HNO₃
4M
80°C

Débit 120 mL/H



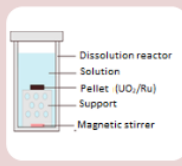
- Increase of the UO₂ dissolution rate in the presence of Ru (potential impact of UO₂ grains size ?)
- Analyses of C_{Ru} by ICP-MS :dissolution of 70 wt.% of Ru particles

- [U]=[HNO₂] : equimolar proportion
→ Low impact of Ru on [HNO₂]

→ Autocatalyzed mechanism of dissolution with or without Ru

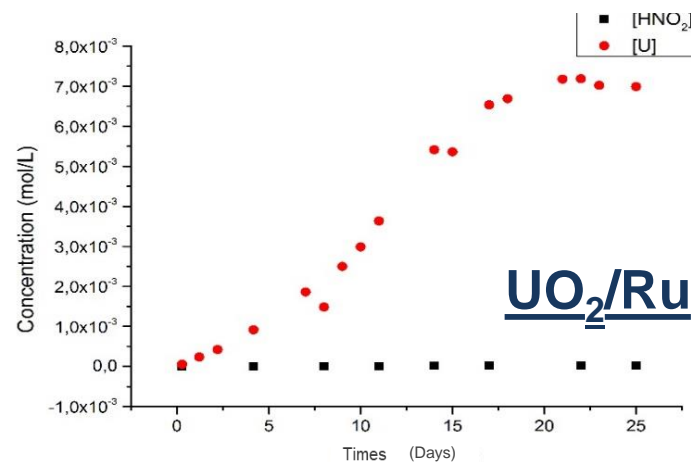
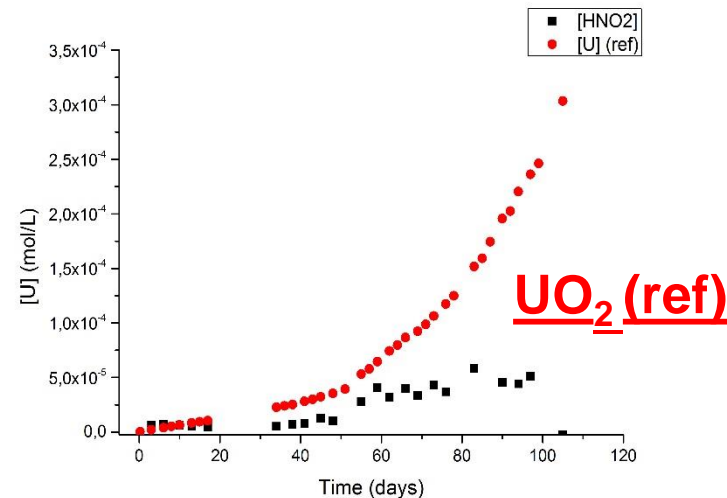
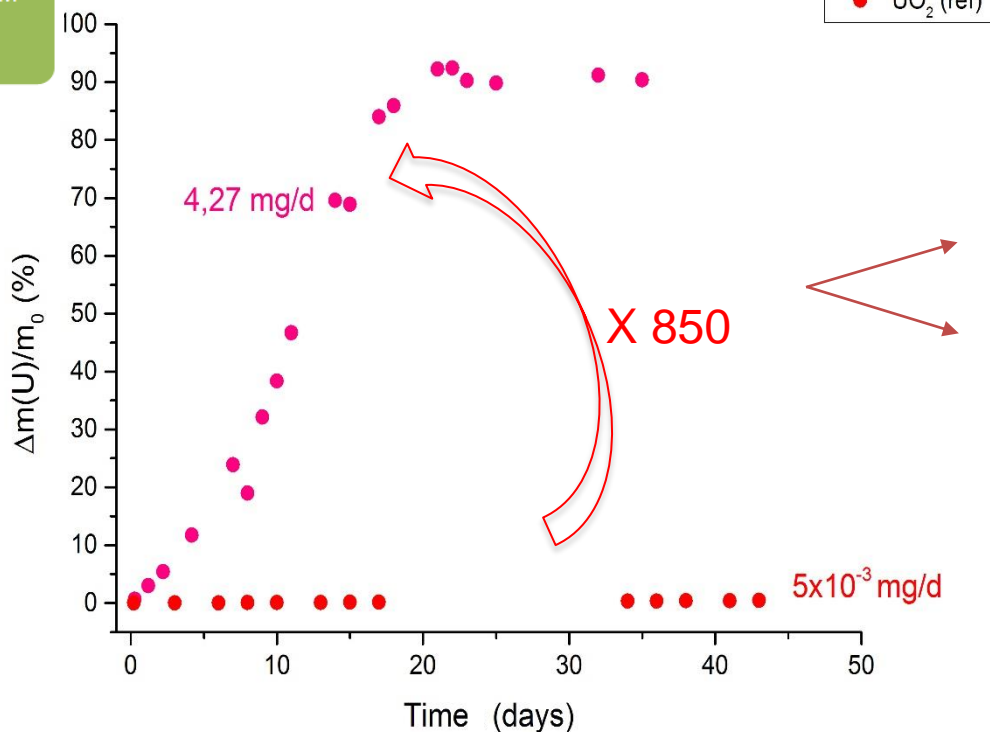
→ low impact of Ru on the dissolution rate

UO₂/Ru (3%mol) 0.1M HNO₃ 60°C



UO₂/Ru
(3%mol)

HNO₃ 0,1M
HCl 0,1M
60°C



- Presence of Ru:

- Strong increase of UO₂ dissolution rate ($\times 850$)
- Very low dissolution of Ru particles ($< 2\%$)

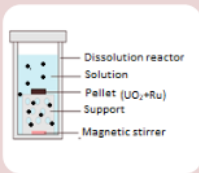
- [U]/[HNO₂] : non-equimolar proportion

- For UO₂/Ru, HNO₂ is not responsible for increase of UO₂ dissolution rate

In 0,1M HNO₃ UO₂ dissolution is not catalyzed by HNO₂

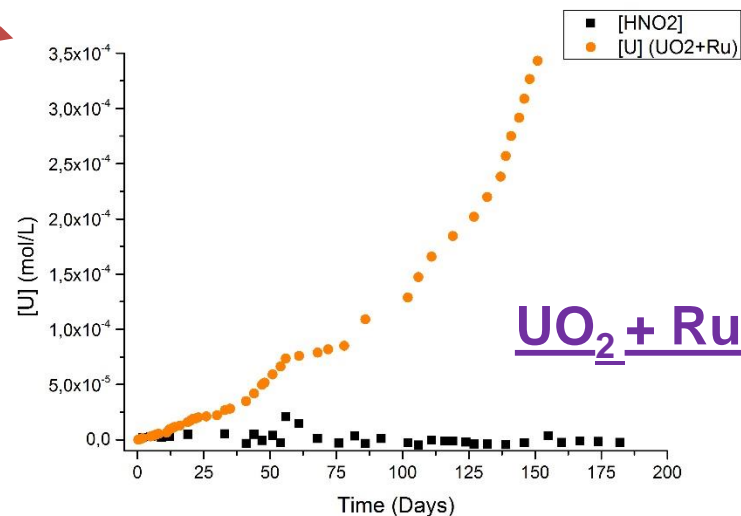
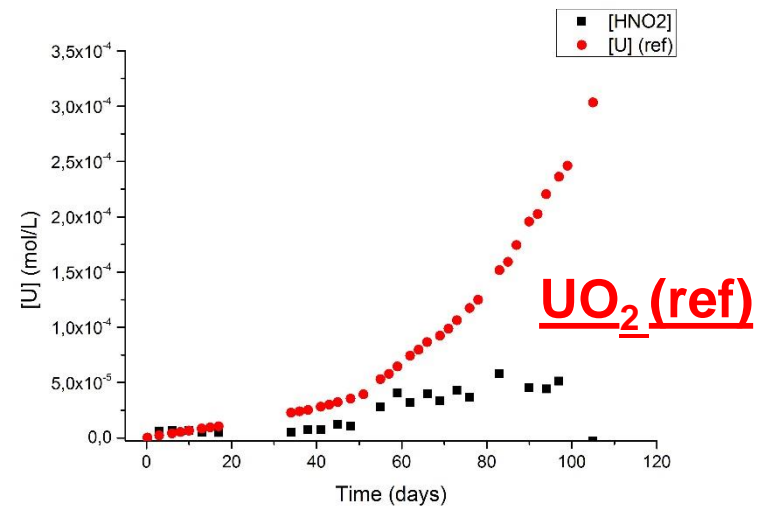
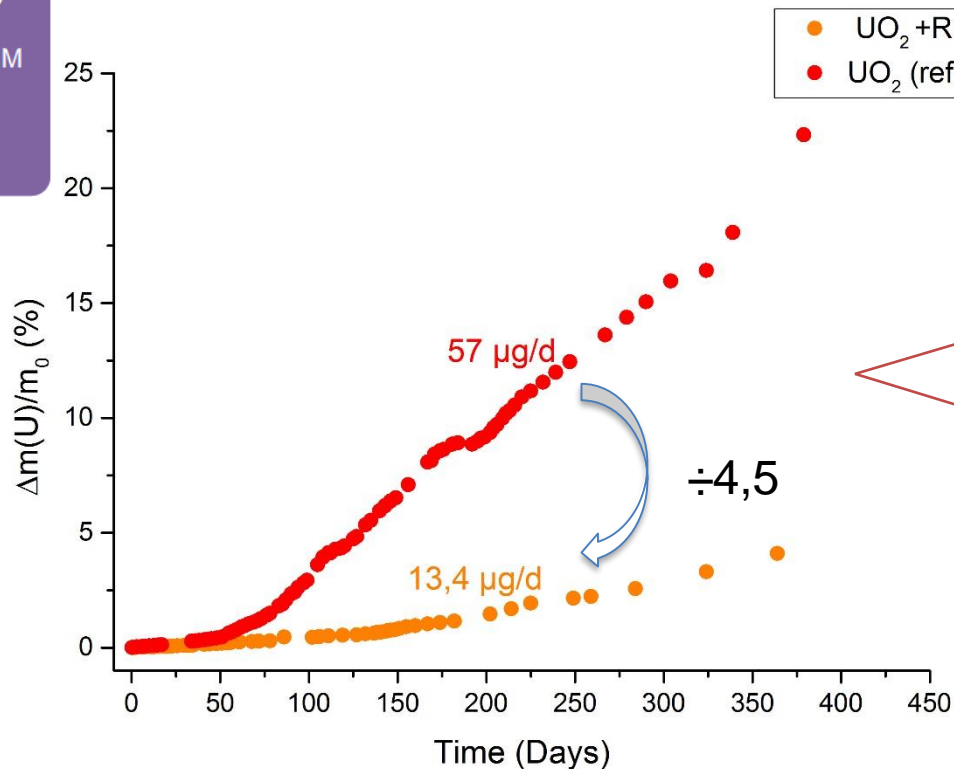
Metallic particles of Ru catalyse the dissolution (similar result obtained in 0,1M HCl)

UO₂ + Ru in 0.1M HNO₃ 60°C



UO₂ + Ru
(3%mol)

HNO₃ 0,1M
60°C



- Presence of Ru particles in suspension: decrease of the dissolution rate of UO₂ (÷ 4,5)

- [HNO₂] close to DL ($\approx 10^{-6}$ mol/L) even lower than in absence of Ru particles

Ru particles in suspension decompose HNO₂, therefore the dissolution of UO₂ slows down.

- Different behaviour depending on the location of Ru:
 - UO_2/Ru : Ru particles in contact with UO_2 grains catalyse the dissolution
 - $\text{UO}_2 + \text{Ru}$: Ru particles in suspension in HNO_3 solution decompose HNO_2 , which inhibits the transition to auto-catalysed mechanism

- High complexity of Ru chemistry with 8 different D.O.s
 - possible reactions between U(IV) and Ru / between HNO_2 and Ru at particles / solution interface

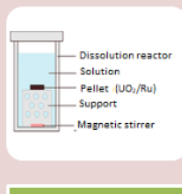
- Further experiments dedicated to the role of Ru (III) dissolved species

 Is the oxidative dissolution of Ru particles necessary to catalyse UO_2 dissolution ?



**Thank for your
attention !**

UO₂/Ru (3%mol) 0.1M HCl 60°C



UO₂/Ru
(3%mol)

HNO₃ 0,1M
HCl 0,1M
60°C

