Fabrication of (U,Ce)O_2 and (U,Am)O_2 pellets with controlled porosity from oxide microspheres

L. Ramond, P. Coste, M. Bataille, S. Picart, A. Gauthe

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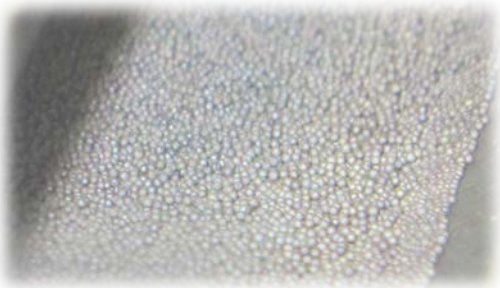
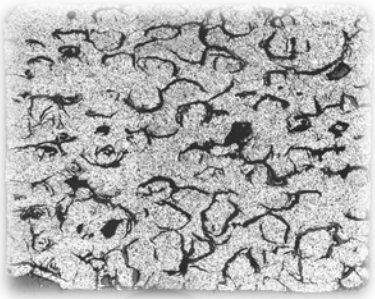
L. Ramond[1], P. Coste[1], M. Bataille[1], S. Picart[2], A. Gauthé[2]

[1] DEN/DTEC/SECA/LFC

[2] DEN/DRCP/SERA/LCAR





14 IEMPT, 17-20 october 2016

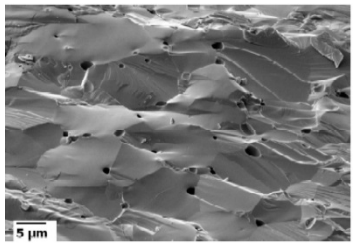
DEN **D**irection de l'**É**nergie **N**ucléaire
DTEC **D**épartement de **TE**chnologie du **C**ycle du combustible
SECA Service d'Etudes des Combustibles et matériaux à base d'Actinides
LFC **L**aboratoires de Fabrication des Combustibles

GOAL OF THE STUDY

- Fabrication of $(U,Am)O_2$ heterogeneous targets (10-15%Am) called MABB for the periphery of the core - framework of GEN-IV international forum
- Test of minor actinide bearing fuels behavior fabricated by metallurgical process:
  - MARIOS : 15% Am porous (88%) and dense (92%)
  - DIAMINO : 7,5/15at.% Am (DIAMINO) (porous: 82-85% and dense: 96-97%)
- Assess the influence of the fuel microstructure on the **helium release**

  => Comparison between **dense / tailored porosity** pellets

Innovative process
WAR microspheres + CRMP



- Fabrication of dense pellet $(U,Am)O_2$ demonstrated in 2013
- Fabrication of porous pellet $(U,Am)O_2$ from oxide microspheres needs to be demonstrated (D~86-90%, open porosity >8%)
- Low quantity of U-Am-O microspheres available for R&D, necessary to use a surrogate (U-Ce-O)

FABRICATION OF DENSE $U_{1-x}Am_xO_{2\pm\delta}$ PELLETS : PROCESSES DEVELOPED AT CEA

2010

Reactive sintering between UO_2 and AmO_2

UO_2 AmO_2

Simplicity

Incomplete densification <92%

2011

UMACS, adding of a step dedicated to solid solution formation

UO_2 AmO_2

High densities >95%

Dust production

2013

Use of $U_{1-x}Am_xO_{2\pm\delta}$ CO-CONVERTED powder as a precursor

Solid solution $(U,Am)O_2$

High densities >95%
Reduced sintering temperature

Reduced dust production

Calcined Resin Microsphere pelletizing

Impregnation of resin microspheres with U/Am nitrate

High densities >95%

Highly reduced dust production

Improvment of the densification

Reduction of dust generation, increase of reactivity (fine grains)

D. Prieur *et al.*, *J. Nucl. Mater.* **414** (2011) 503

T. Delahaye et al., French patent 11–60597, 2011 // *J. Nucl. Mater.* **432** (2013) 305

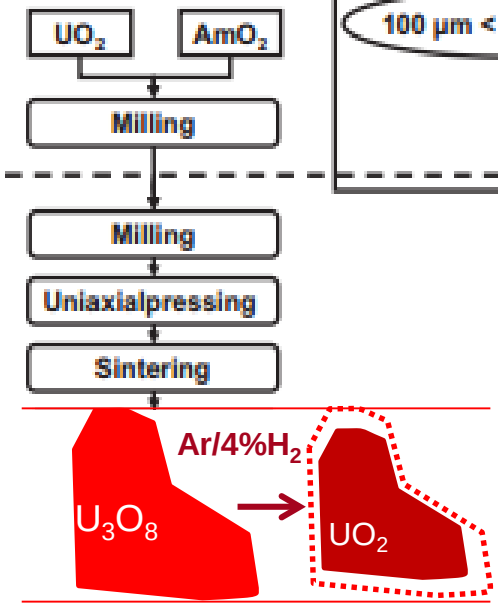
D. Horlait *et al.*, *J. Nucl. Mater.* ***444*** *(2014) 181*
L. Ramond et al., JECS 36 (2016) 1775

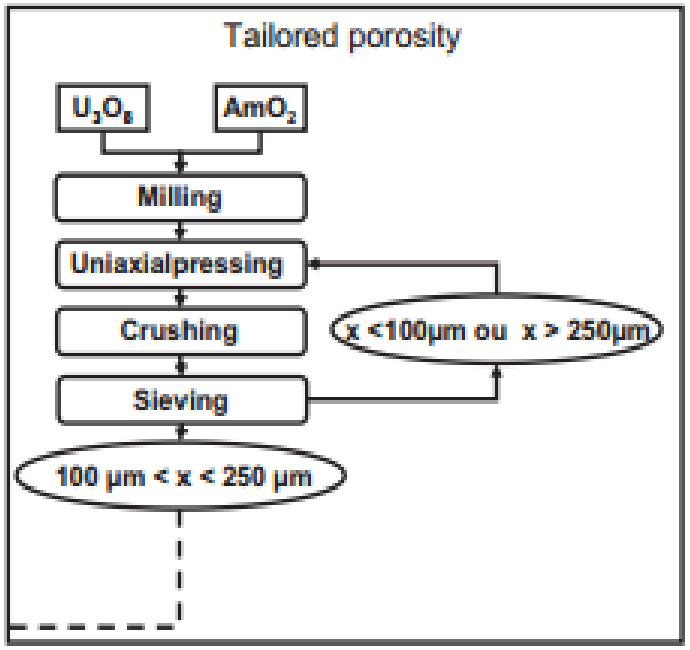
E. Remy *et al.*, *J. Nucl. Mater.* **453** (2014) 214

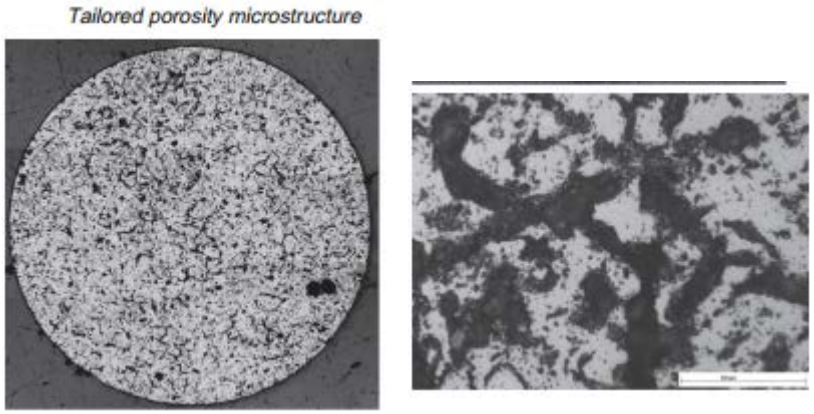
FABRICATION OF POROUS $U_{1-x}Am_xO_{2\pm\delta}$ PELLETS : REACTIVE SINTERING BETWEEN UO_2, U_3O_8 AND AmO_2

2011-2013

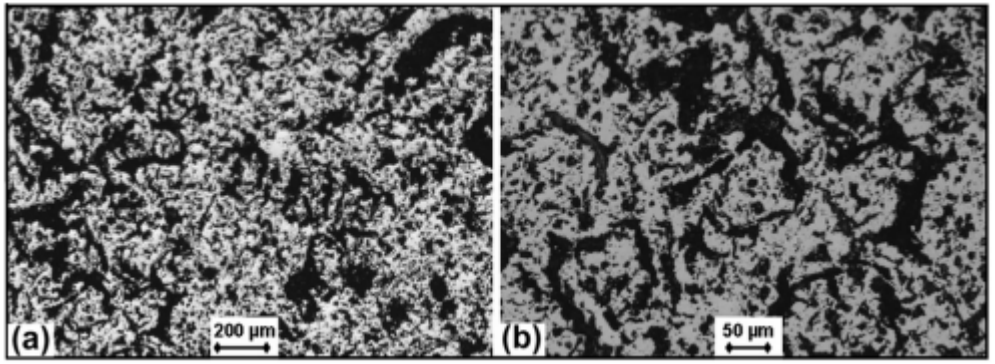
Dust production due to granulation steps







MARIOS $U_{0.85}Am_{0.15}O_{2\pm\delta}$



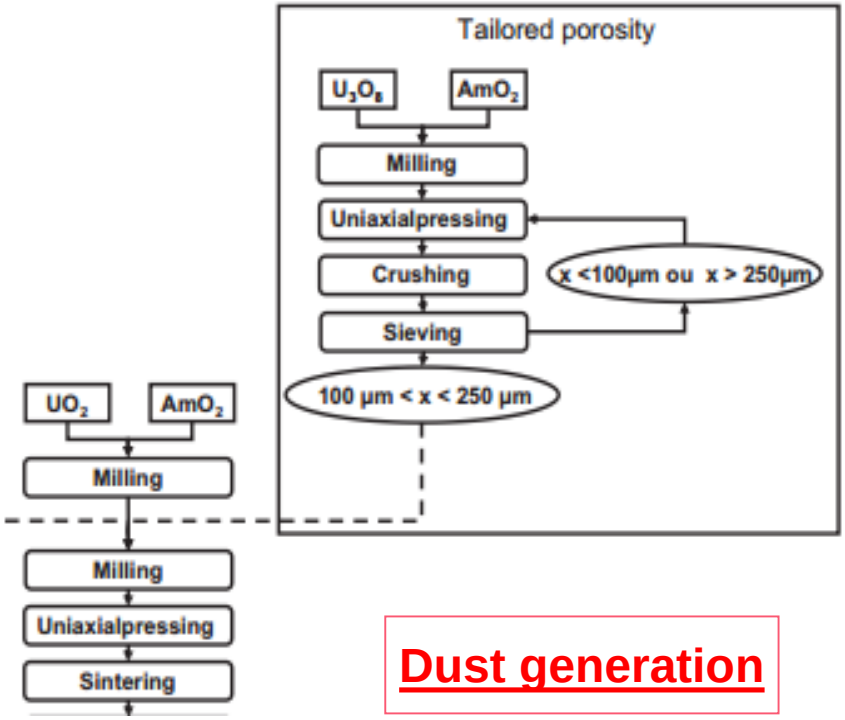
DIAMINO $U_{0.925}Am_{0.075}O_{2\pm\delta}$

D. Prieur *et al.*, *J. Nucl. Mater.* **414** (2011) 503
T. Delahaye, J. Nucl. Mater. 432 (2013) 305

FABRICATION OF POROUS $U_{1-x}Am_xO_{2\pm\delta}$ PELLETS : INNOVATIVE PROCESS

2011-2013

Reactive sintering between UO_2, U_3O_8 and AmO_2



Dust generation

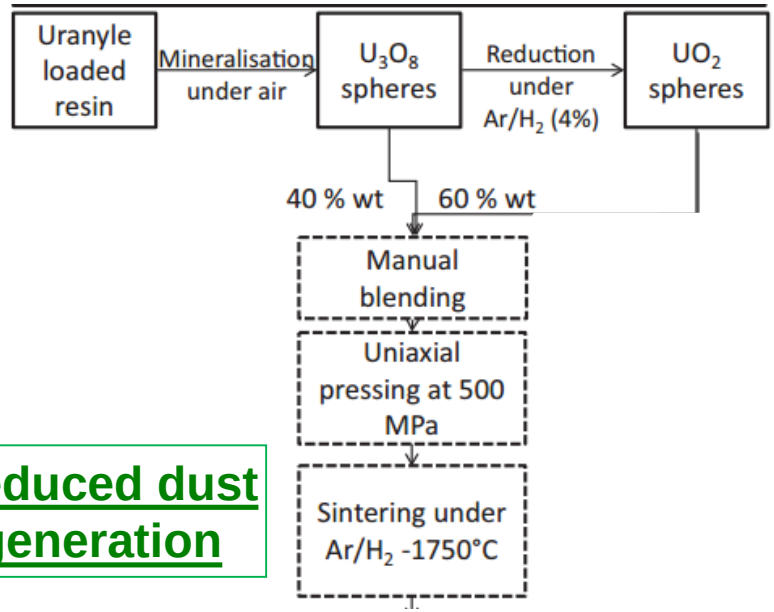
Porous pellets 82-87%TD
Open porosity >8%

D. Prieur *et al*., *J. Nucl. Mater.* **414** (2011) 503
T. Delahaye, J. Nucl. Mater. 432 (2013) 305

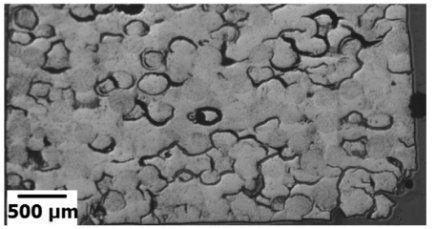
2013-2014

ONLY UO_2

Calcined Resin Microsphere Pelletizing



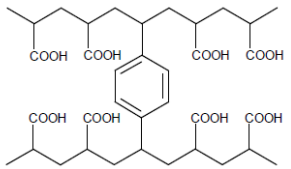
Reduced dust generation



E. Remy *et al*. (*J. Nucl. Mater.* **448** (2014) 80)

U-Ce-O MICROSPHERES SYNTHESIS (WAR PROCESS)

Resin → **Sieving - washing** → **Fixation** → *Filtration*



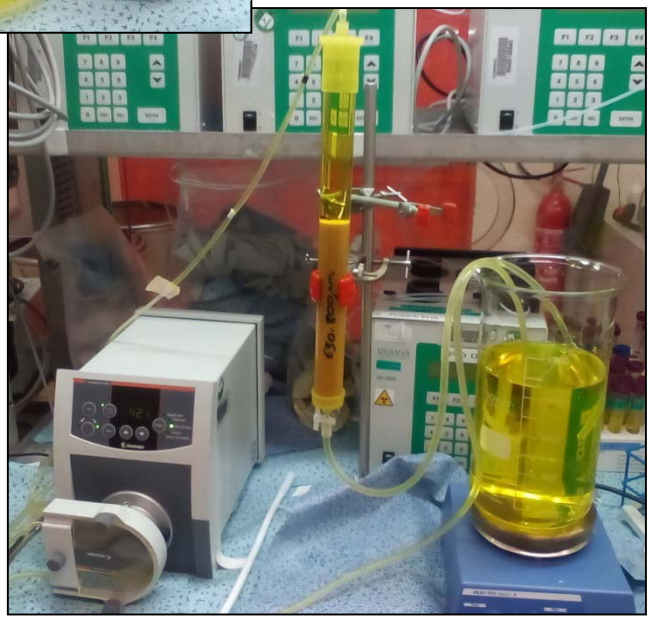
weak acid cation exchange resin : IMAC HP333 carboxylic resin (Dow Chemicals)

30g [630-800µm] $HNO_3/H_2O/NH_3/H_2O/…HNO_3/H_2O$

Impregnation by recirculation (6h)

Solution

Water + HNO_3 + UO_3 + $Ce(NO_3)_3,6H_2O$
target -> 15at.%Ce in oxide



Impregnation

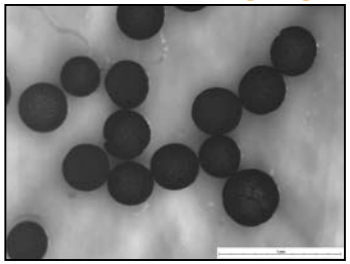
- Weight of the dried loaded resin: 50g
- Chemical analysis on dissolved loaded resin: [Ce/(U+Ce)] = 13.8 at.% Ce

U-Ce-O MICROSPHERES SYNTHESIS (WAR PROCESS)

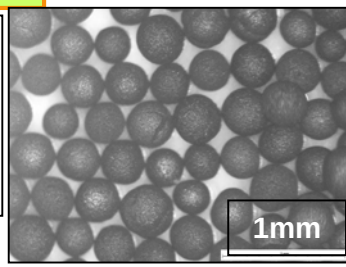
Fixation → **Drying** → **Carbonisation under air** → $(U,Ce)_3O_8$ → **Reductive treatment Ar/4%H_2** → $(U,Ce)O_2$

105°C
1 night

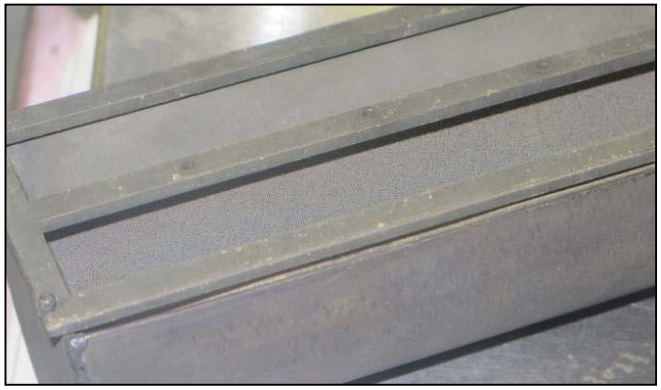
700°C - 4h
heating rate:
1,5°C/min
Δm=56%



700°C - 5h
heating rate:
10°C/min
Δm=-4%



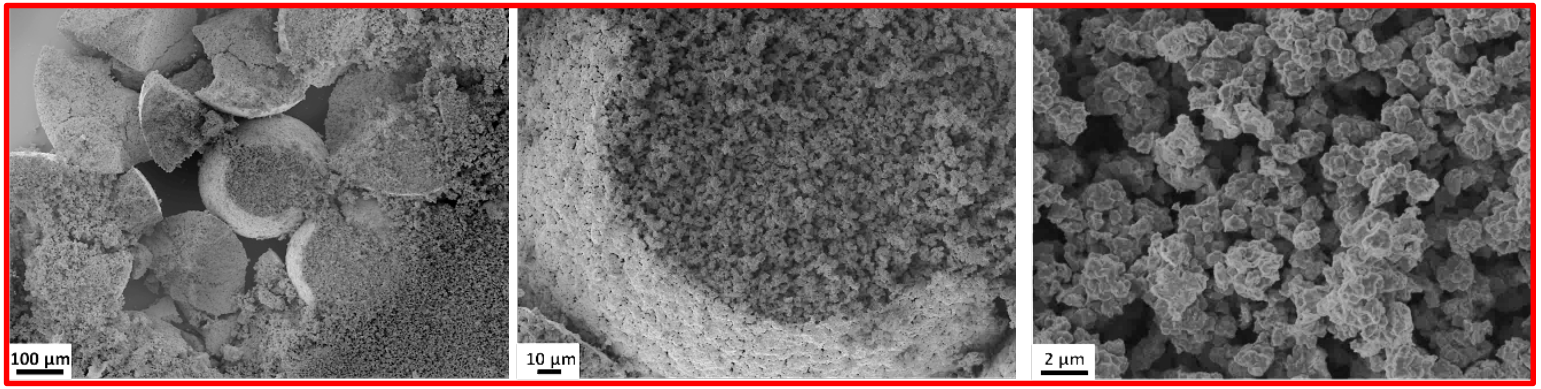
Dried loaded resin microspheres before calcination **50g**

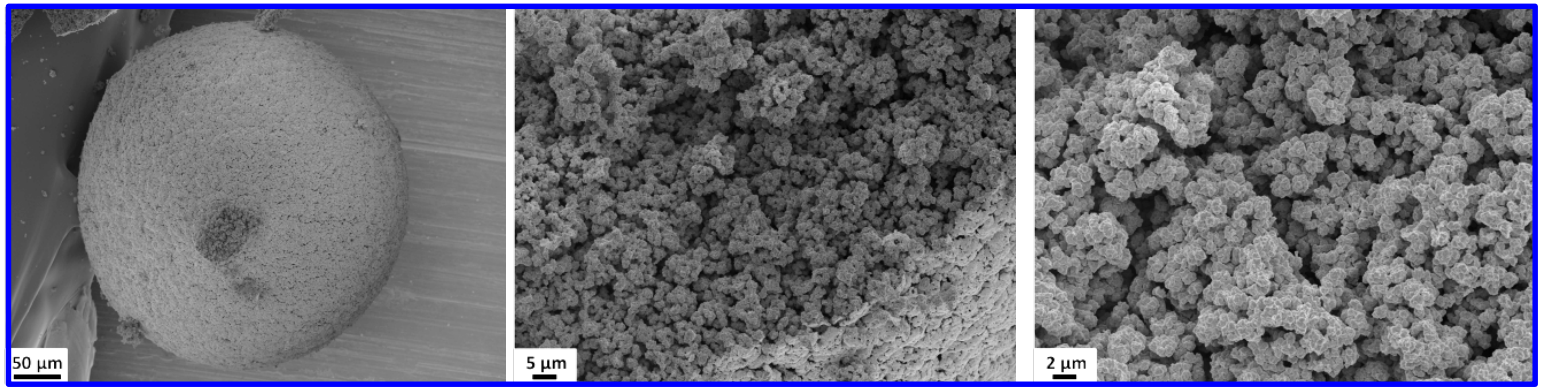


Microspheres after calcination under air **22g**.(-56%)

Synthesis of 9g $(U,Ce)_3O_8$ + 13g $(U,Ce)O_2$ microspheres

MICROSTRUCTURE

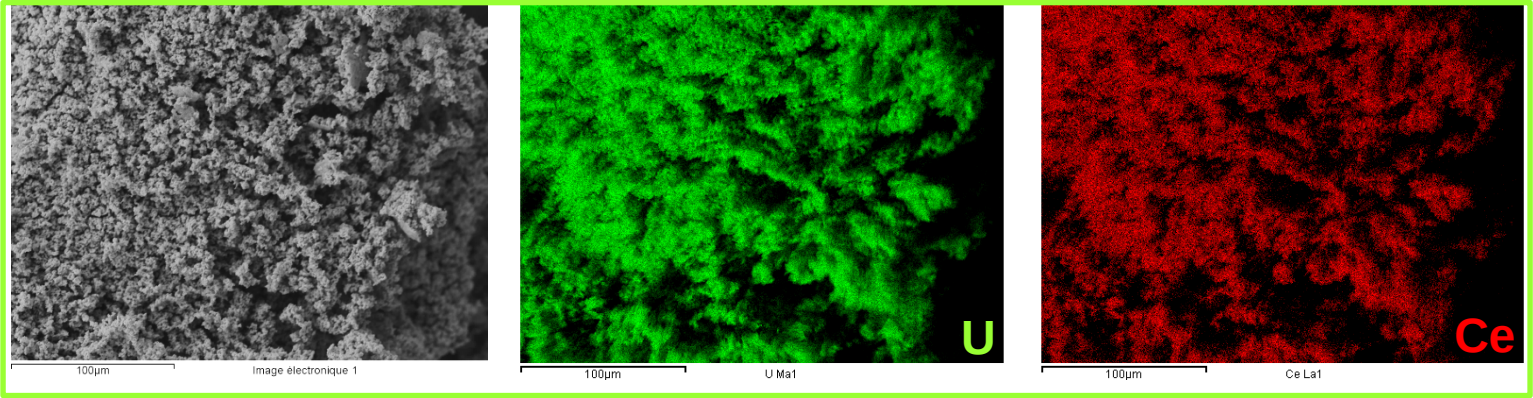




$(U,Ce)_3O_8$

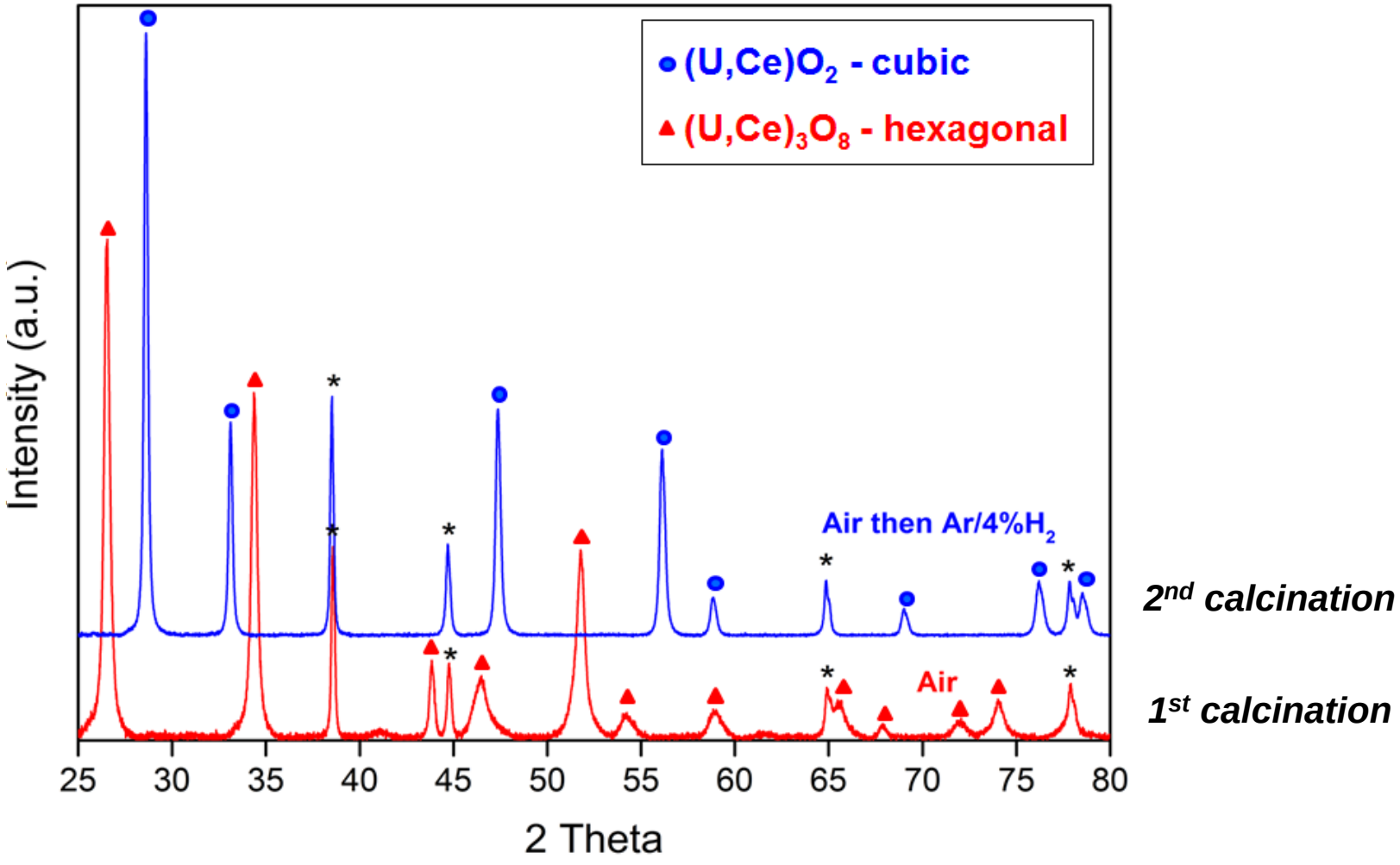
Porous microstructure after calcination under air as well as after the second heat treatment under Ar/4vol.%H_2

$(U,Ce)O_2$



Energy dispersive spectroscopy revealed homogeneity of U and Ce distributions between microspheres.

EVOLUTION OF THE STRUCTURE WITH THE ATMOSPHERE OF CALCINATION

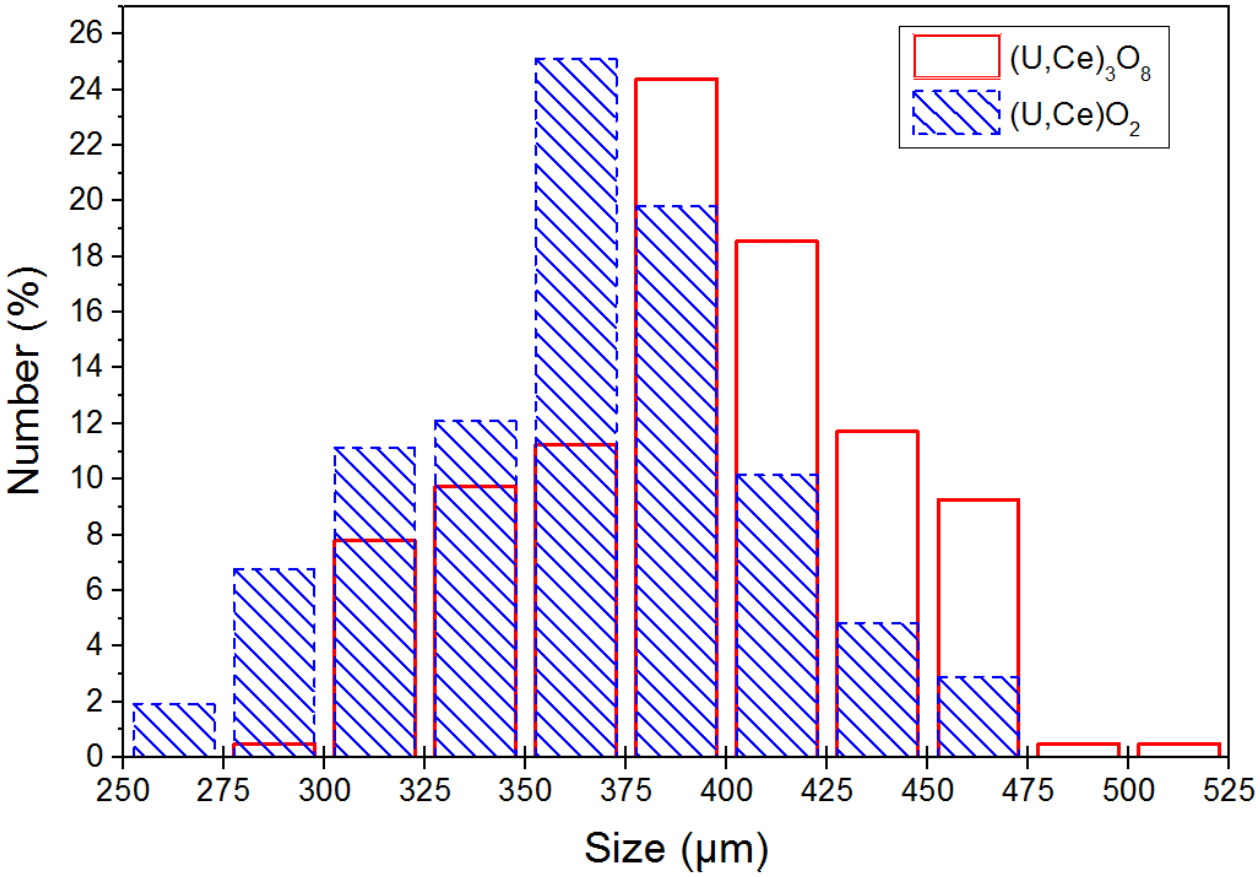


2nd calcination

1st calcination

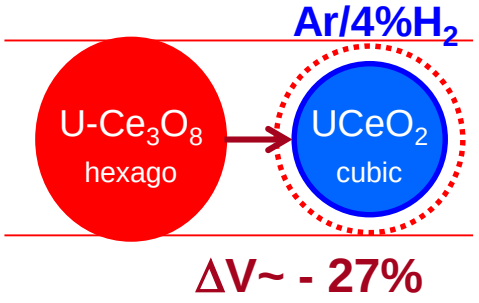
EVOLUTION OF THE DIAMETER WITH THE STRUCTURAL CHANGE

3% decrease of the lattice volume (hexagonal -> cubic) => leads to microsphere compaction



D_{av} $(U,Ce)_3O_8$ ~ 400 µm

D_{av} $(U,Ce)O_2$ ~ 360 µm



FABRICATION OF POROUS PELLET $(U,Ce)O_2$

U/Ce loaded resin

Air

$(U,Ce)_3O_8$ spheres

Ar/H_2

$(U,Ce)O_2$ spheres

30/35/40 wt.%

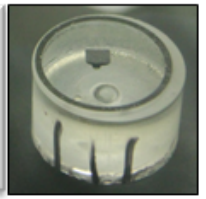
70/65/60 wt.%

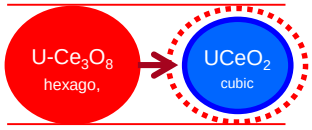
Manual mixing

Uniaxial pressing 700 MPa

Sintering $Ar/4\%H_2$

Cutting Impregnation Polishing

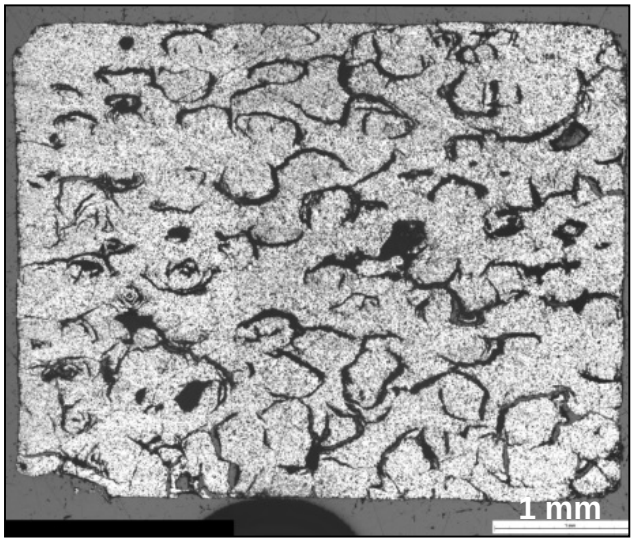




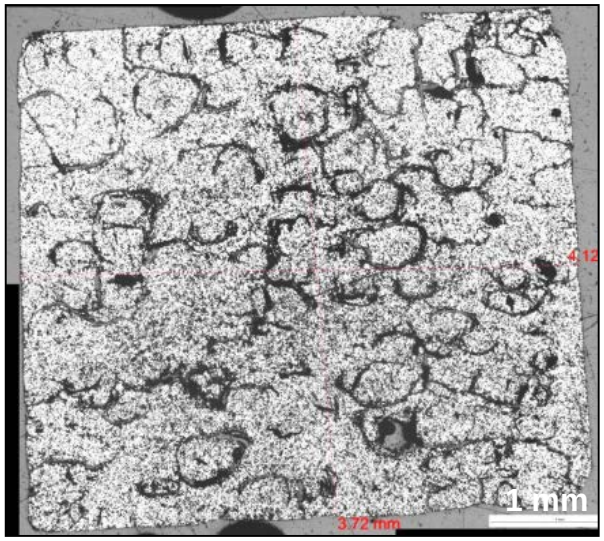
ΔV~ - 30%

OPTICAL MICROSCOPY ON SINTERED PELLETS

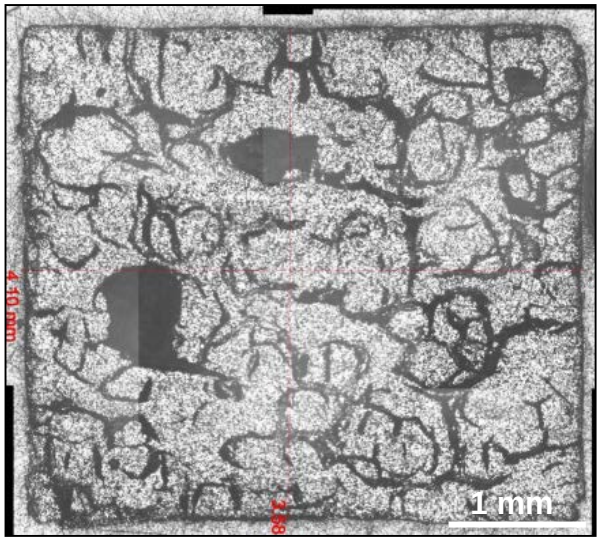
30% $(U,Ce)_3O_8$ - D_{rel}~88%



35% $(U,Ce)_3O_8$ - D_{rel}~89%



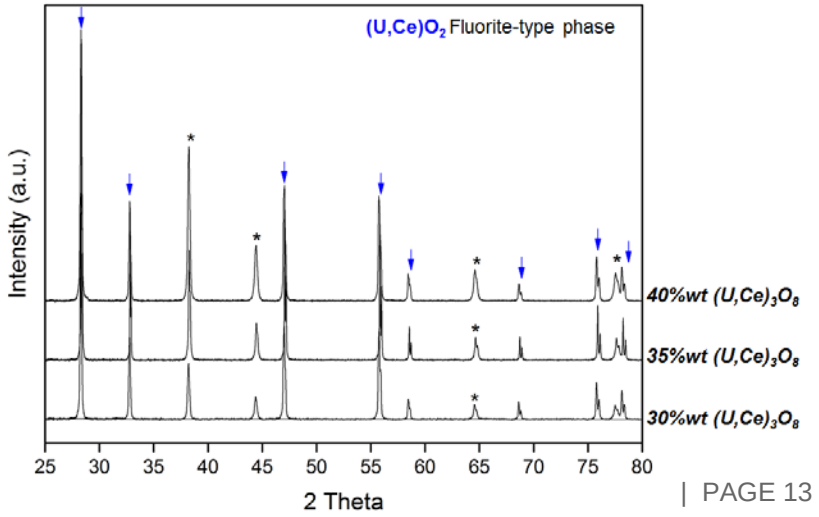
40% $(U,Ce)_3O_8$ - D_{rel}~86%



Interconnected hemispherical porosity => open porosity network

Targeted density 86-90% -> OK for 30-35-40wt.% $(U,Ce)_3O_8$ but for 40% a lower mechanical resistance (grains removal during polishing) -> Selection: 30-35wt.%

=> Demonstration of the $(U,Ce)O_2$ porous pellet fabrication feasibility



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FABRICATION OF $(U,Am)O_2$ POROUS PELLET

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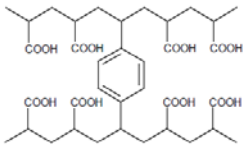
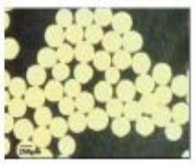
U-Am-O MICROSPHERES SYNTHESIS (HOT CELL)

Resin → **Sieving - washing** → **Fixation** → **Drying** → **Carbonisation under air** → **Reductive treatment Ar/4%H_2**



weak acid cation exchange resin : IMAC HP333 carboxylic resin (Dow Chemicals)

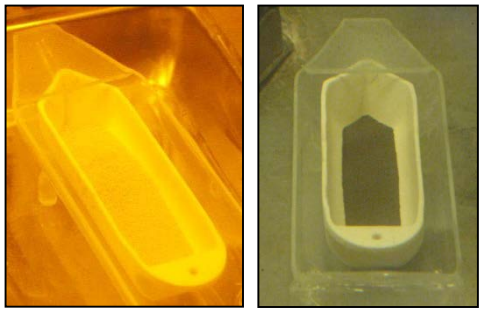


50g [630-800µm] $HNO_3/H_2O/NH_3/H_2O/\ldots HNO_3/H_2O$

Impregnation by recirculation (5h)

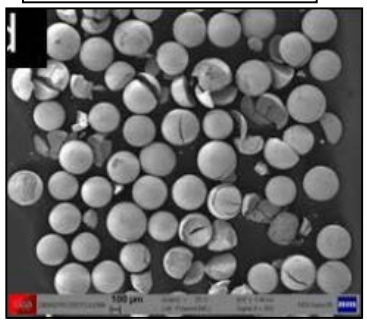
105°C
1 night

700°C - 4h
heating rate: 1,5°C/min



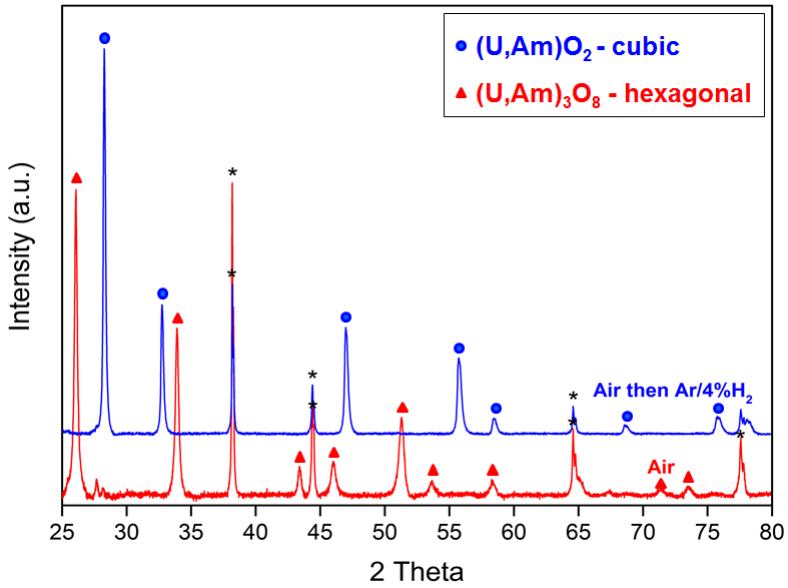
→ $(U,Am)_3O_8$

700°C - 5h
heating rate: 10°C/min



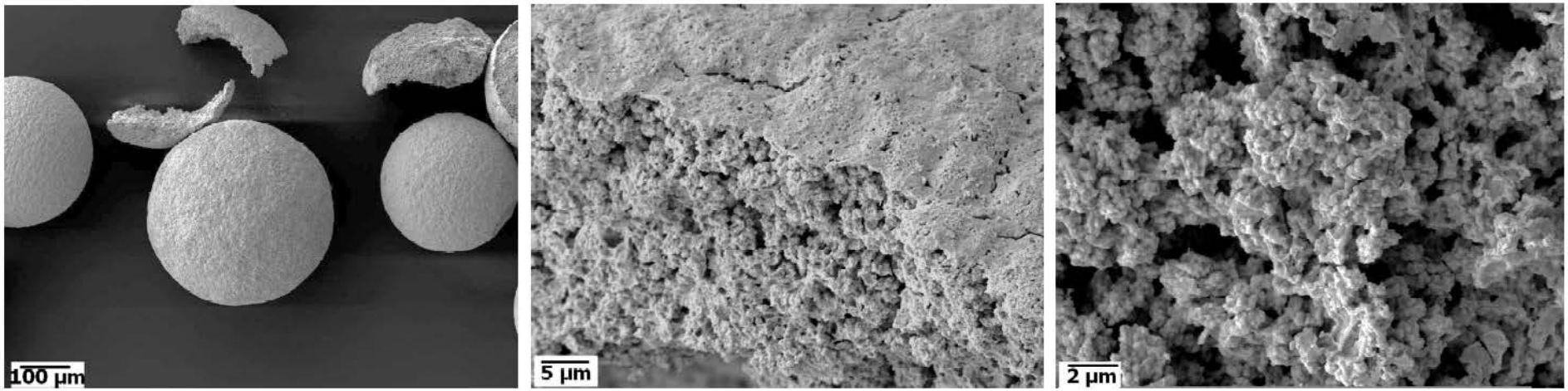
→ $(U,Am)O_2$

Demonstration of feasibility
DRCP/SERA/LCAR :
2013 : 6g 11%at. Am
2015 : 27g 15%at. Am



CHARACTERIZATION OF (U,Am)O_2 MICROSPHERES

- **Single-phase (fluorine type) (XRD)**
- **Carbon content before sintering : 1900 ± 120 ppm**
- Porous microspheres (density ~25%DT) constituted by submicronic particles.
- ∅ ~375 µm

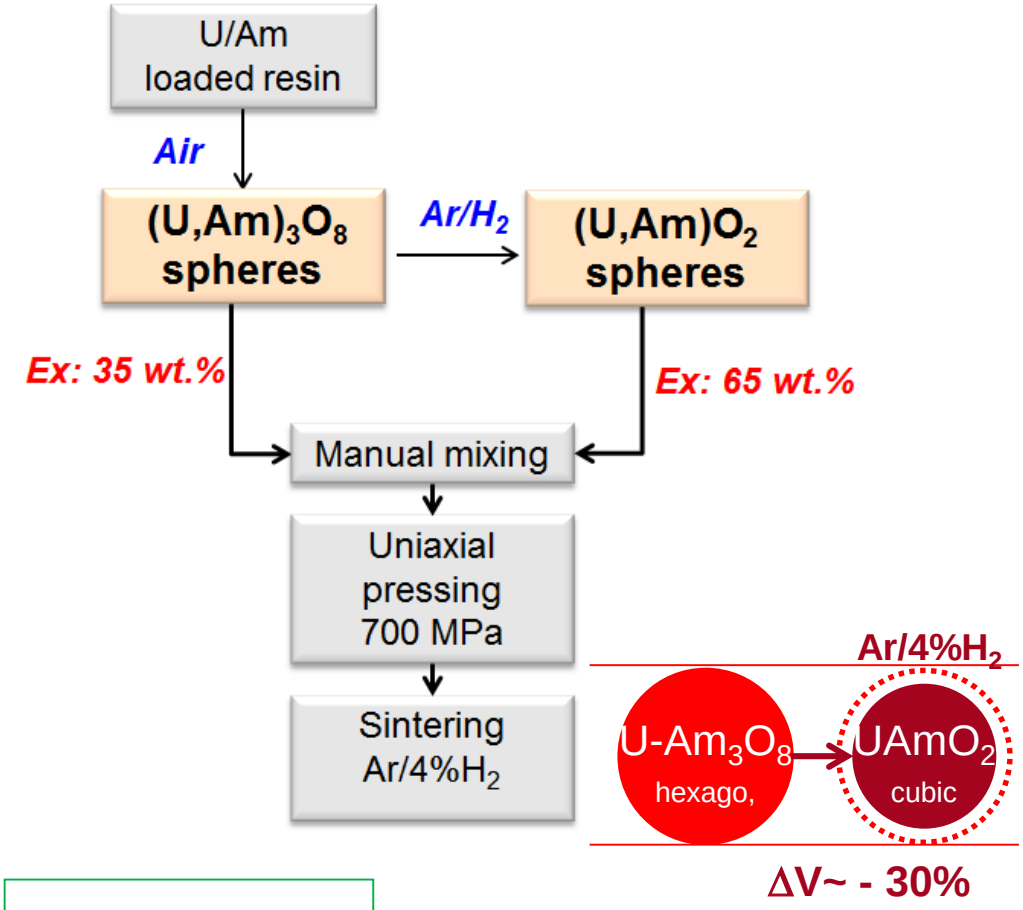


SEM micrographs in secondary electron mode showing reduced oxide microsphere morphology and internal microstructure

FABRICATION OF POROUS $U_{0.89}Am_{0.11}O_{2\pm\delta}$ PELLETS: CALCINED RESIN MICROSPHERE PELLETIZING

2016

Calcined Resin Microsphere pelletizing

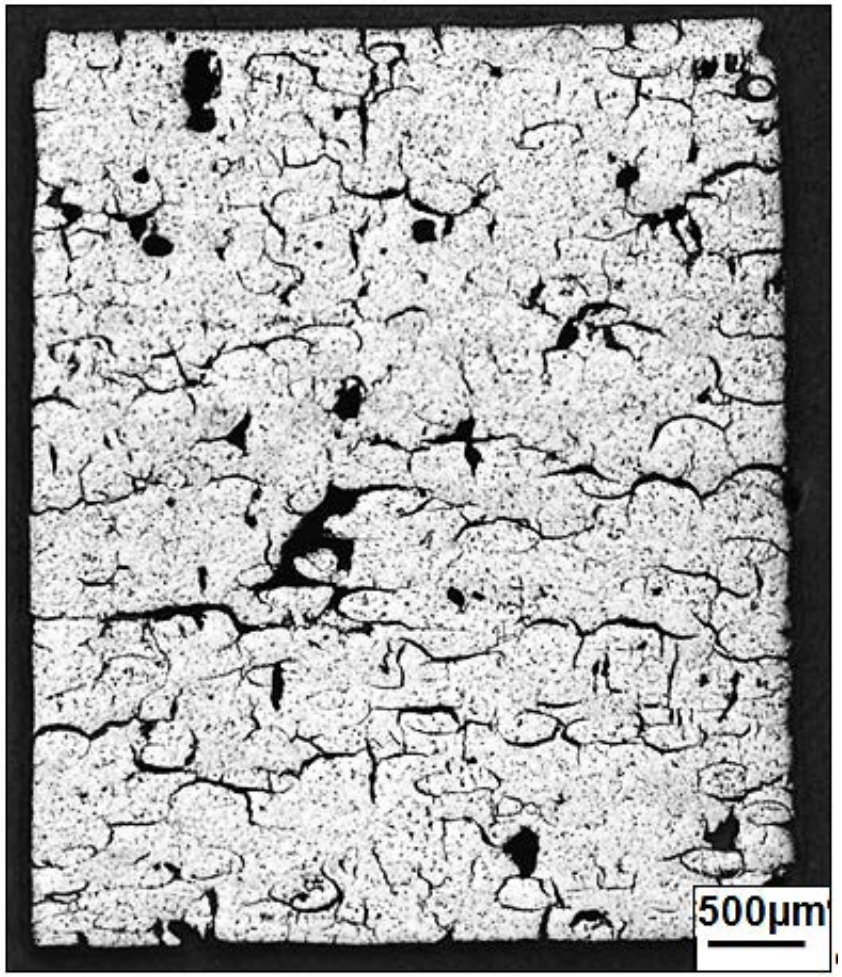


Porous pellet requirements

- Density 86-90%TD
- Open porosity >8%

Reduced dust production

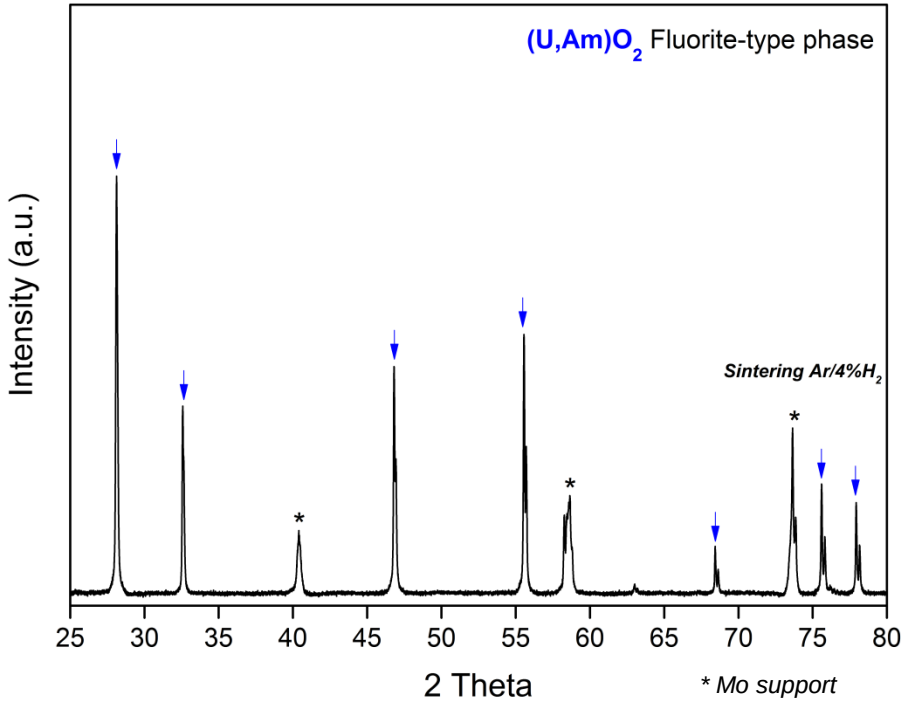
FABRICATION OF POROUS $U_{0.9}Am_{0.1}O_{2\pm\delta}$ PELLET: CALCINED RESIN MICROSPHERE PELLETIZING



Optical microscopy - $U_{0.90}Am_{0.10}O_{2\pm\delta}$

Final porous pellet

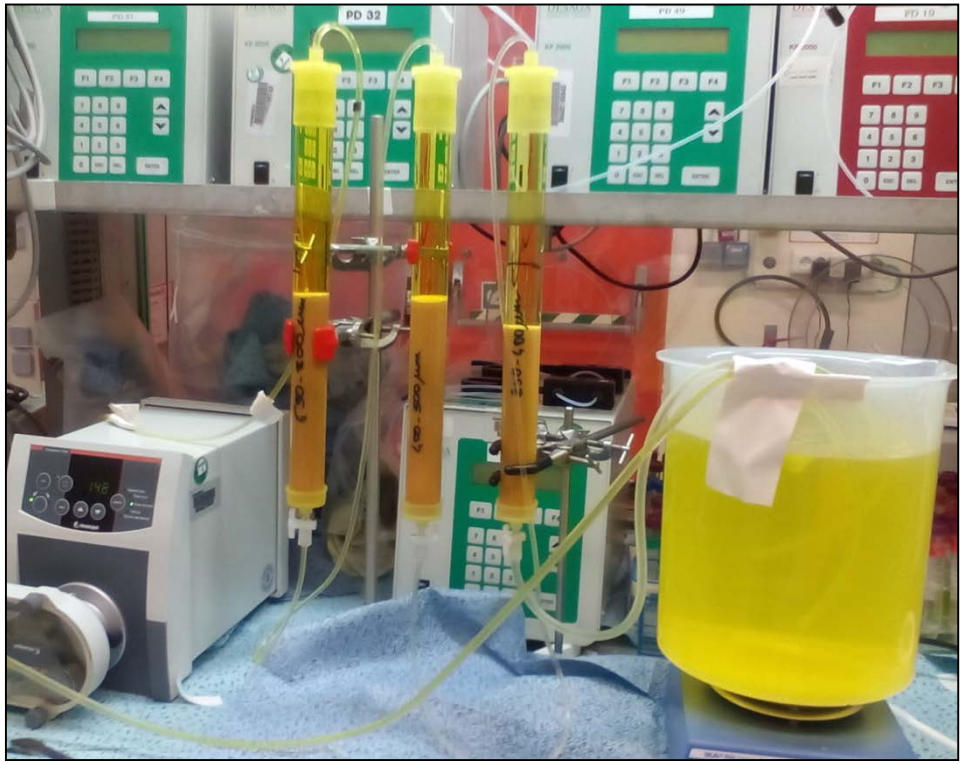
- **Density 89%TD (86-90)**
- **Open porosity =9% (>8)**
- **$(U,Am)O_2$ cubic phase**



Interconnected hemispherical porosity => open porosity network

CONCLUSION - PERSPECTIVES

- Demonstration of the fabrication of $(U,Am)O_2$ pellet with controlled porosity from oxide microspheres
- Dustless process (no production of fine particles, no milling, only pelletizing and sintering)
- Perspectives: optimisation of the tailored porosity by modifying the resin beads size



3 size ranges:

[630-800µm]

[400-500µm]

[250-400µm]

About 20g of U/Ce oxide microspheres for each granulometry

AKNOWLEDGEMENTS

DEN/DTEC/SECA/LFC

DEN/DTEC/SECA/LCC

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DEN/DRCP/SMCS/LDPS : X Hérès, D Sans, M Bertrand

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