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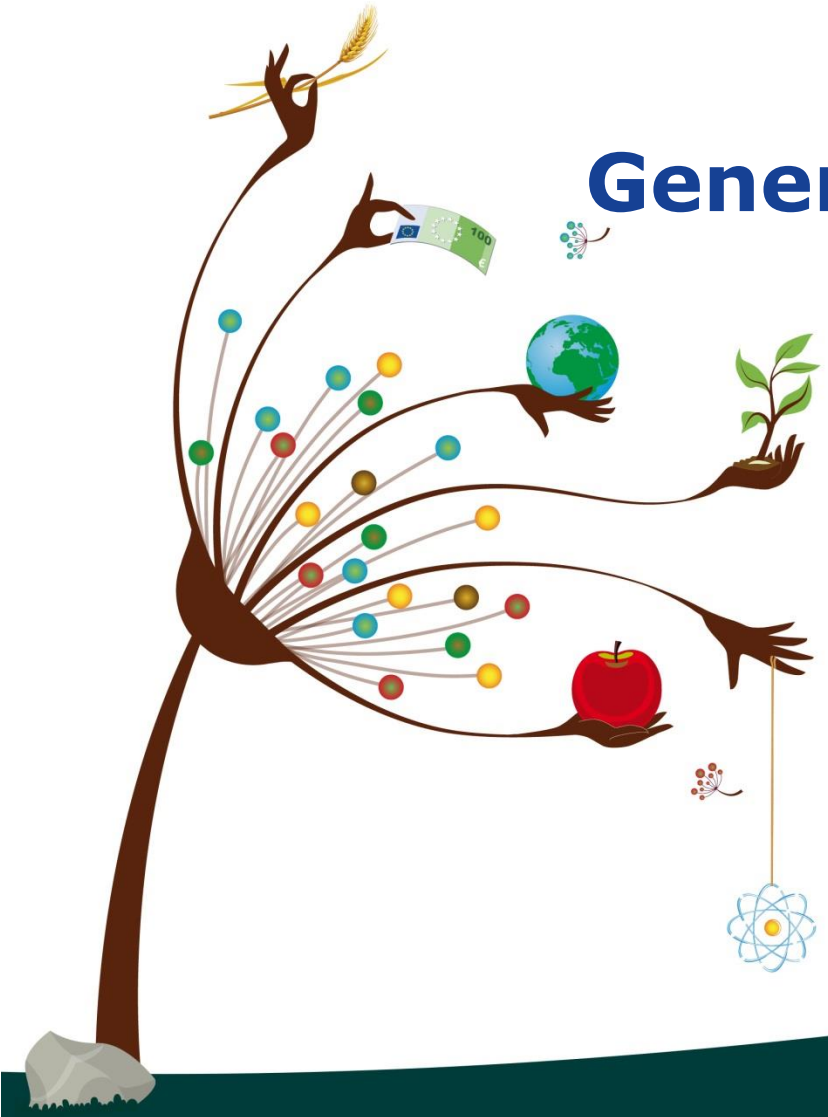

Generation IV advanced fuel fabrication routes.

Part I

13.05.2019, Delft

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Generation IV and fusion fuel fabrication routes.

Part I

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European Commission

Criteria for fuel materials

- ✓ Low neutron capture cross section of non-fissile elements
- ✓ High fissile density
- ✓ No chemical reaction with cladding or coolant
- ✓ Favorable physical properties, especially thermal conductivity and melting point (*together give the margin to melting*)
- ✓ High mechanical stability (*isotropic expansion, stable against radiation*)
- ✓ High thermal stability (*no phase transitions, no dissociation*)

Summary of designs for generation IV reactors

System	Neutron spectrum	Fuel cycle	Fuel (+MA)	Fuel form	Coolant
Very-high-temperature reactor (VHTR)	Thermal	Open	UO_2,UCO PuO_2 $(Zr,Y,Pu)O_2$	Coated particle	Helium
Sodium-cooled fast reactor (SFR)	Fast	Closed	$(U,Pu)O_2$ MC/MN Targets	Pellet (Sphere Pac)	Sodium
Supercritical-water-cooled reactor (SCWR)	Thermal or fast	Open or closed	UO_2, $(U,Pu)O_2$ $(U,Th)O_2$	Pellet	Water
Gas-cooled fast reactor (GFR)	Fast	Closed	MC, MN/ $(U,Pu)O_2$	Disk	Helium
Lead-cooled fast reactor (LFR)	Fast	Closed	$(U,Pu)O_2$ MN	Pellet (Sphere Pac)	Lead
Molten-salt reactor (MSR)	Fast or thermal	Closed	LiF-ThF_4-UF_4	Fluid	Fluoride or chloride salts

Oxide fuels for GenIV reactors

Advantages

- ✓ **Technology already demonstrated!**
- ✓ Fabrication is simple, with less no. of process steps
- ✓ Good chemical stability
- ✓ Can accommodate MA in their structure
- ✓ High melting point
- ✓ Satisfactory chemical compatibility with coolant and cladding materials
- ✓ Industrial-scale experience in oxide spent fuel reprocessing

Oxide fuels for GenIV reactors

Challenges

- ✓ Low thermal conductivity, decreasing with temperature, Pu-content and decreases of pellet density
- ✓ Mechanical pressing and sintering needed
- ✓ Control of oxygen stoichiometry (difficult at high Pu-content and temperature)
- ✓ Accommodation of helium and fission gasses difficult
- ✓ Radiological issues already from the fabrication stage

Sources of fissile/fertile isotopes

- ✓ Thorium
- ✓ Uranium
- ✓ Plutonium
- ✓ Minor actinides

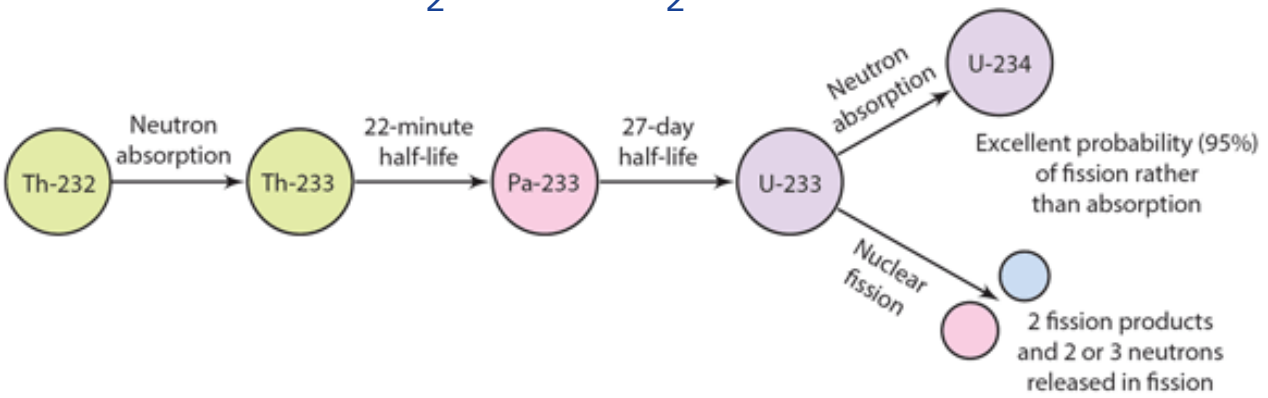
Powder to pellet routes towards UO_2 and mixed oxide fuels

Focus on powder preparation:

- grain size → ease of **sintering**
- dispersion → **homogeneous** microstructure
- shape → **less defects**
- agglomeration → high packing **density**
- chemical composition → **high purity**

Thorium – front end cycle

- ✓ highly reactive and electropositive primordial chemical element
- ✓ estimated to be over three times as abundant as uranium in the Earth's crust
- ✓ virtually monoisotopic, ^{232}Th, has a half-life of 14.05 billion years, or about the age of the universe
- ✓ chemistry is dominated by the +4 oxidation state
- ✓ soluble in concentrated nitric acid (with HF)
- ✓ ThO_2 forms full solid solution with UO_2 and PuO_2



Uranium – front end cycle

PITCH BLEND XUO_2, YUO_2

ORE DRESSING

URANIUM SLURRY

CHEMICAL PROCESSING

$Na_2U_2O_7$+MgU_2O_7

DISSOLUTION IN HNO_3

SOLVENT EXTRACTION with TBP

$UO_2(NO_3)_2$

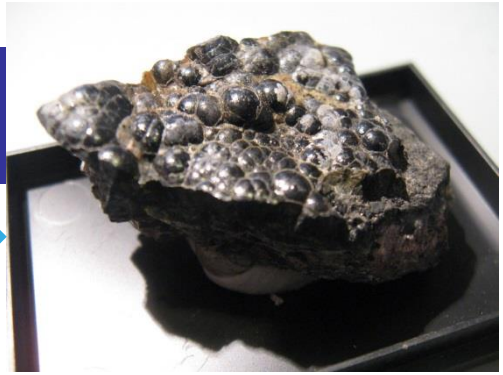
NH_4OH → PRECIPITATE $(NH_4)_2U_2O_7$

CALCINATION

UO_3

REDUCTION

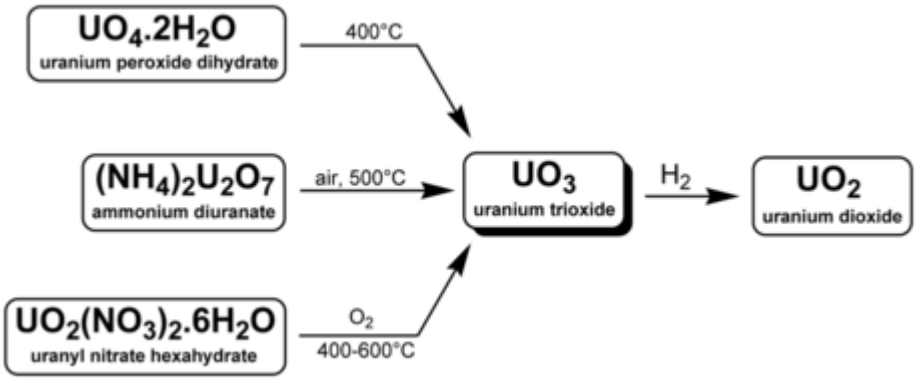
UO_2

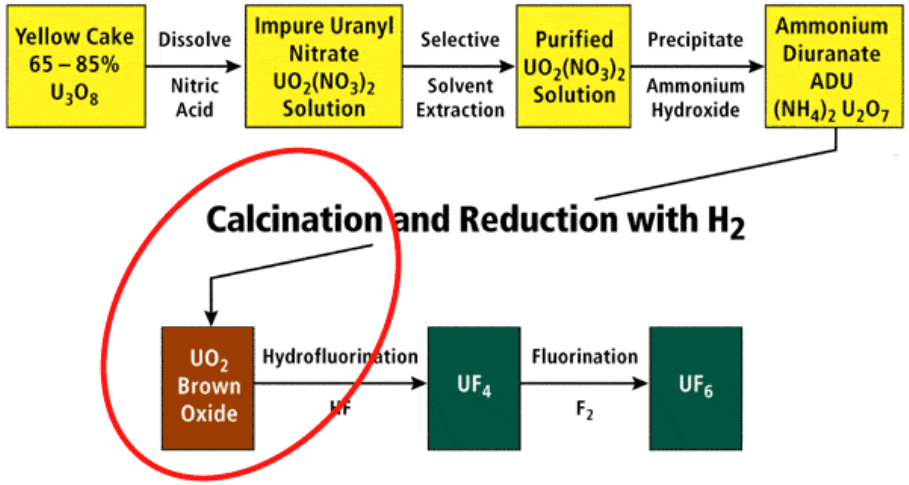


UO_2, Pellets and Fuel Assembly

Uranium – front end cycle

Uranium is stable as U(VI) in aqueous solution.
Electroreduction to U(IV) is not suited at industrial scale, so the oxalate precipitation is not a choice. Several options:





Preparation of ceramic grade UO_2 powder

- All start from UF_6 and end with reduction to UO_2 with H_2

- **IDR (Integrated Dry Route)**

$$UF_6 \xrightarrow{+ H_2O\ (vap)} UO_2F_2\ (s) \xrightarrow{+ H_2O\ (vap)} UO_3 \xrightarrow{+ H_2} UO_2$$

- **ADU (Ammonium Diuranate)**

U precipitated as $(NH_4)_2U_2O_7\downarrow$

- **AUC (Ammonium Uranyl Carbonate)**

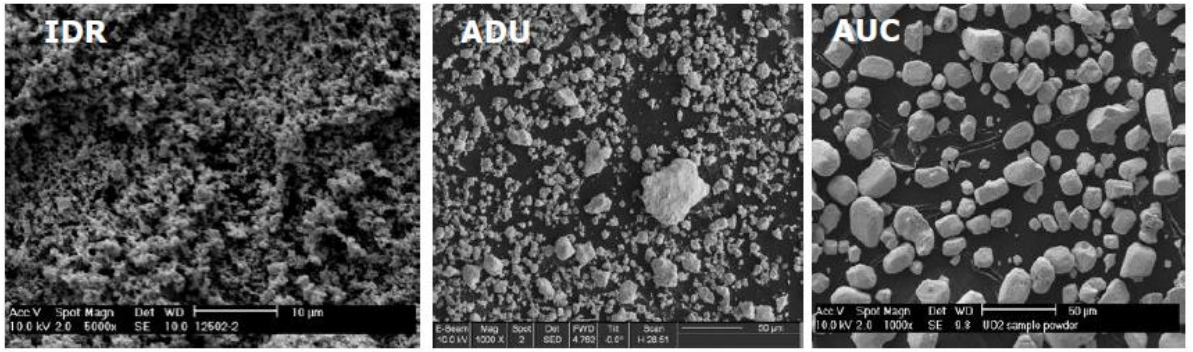
U precipitated as $(NH_4)_4UO_2(CO_3)_3\downarrow$

Dry method

Wet methods

Preparation of ceramic grade UO_2 powder

	IDR	ADU	AUC
Specific surface (m^2/g)	2.5-3.0	2.8-3.2	5.0-6.0
Raw density (g/cm^3)	0.7	1.5	2.0-2.3
Tap density (g/cm^3)	1.65	2.4-2.8	2.6-3.0
Mean size (microns)	2.4	0.4-1.0	8
Morphology	dendrites	spheroids	Porous aggl.
O/U ratio	2.05	2.03-2.17	2.06
Fluor (ppm)	<25	30-50	30-70
Carbon (ppm)	20	40-200	120
Iron (ppm)	10	70	10-20
Boron (ppm)	<0.05	0.2	0.1



Pics: Erik Luther, LANL, LA-UR-12-21451

Nuclear fuel cycle

reprocessing

U mining

High Level Waste

Uranium Storage

Depleted Uranium

Natural Uranium

Enrichment

Processing

repository

Fissile and Fertile

disposal

Spent Nuclear Fuel

SNF Storage

Fuel Fabrication

Reactor

spent fuel storage

nuclear fuels

nuclear reactor

Nuclear fuel cycle – source of fissile/fertile isotopes

reprocessing

U mining

High Level Waste

Uranium Storage

Depleted Uranium

Natural Uranium

Enrichment

Processing

repository

Fissile and Fertile

disposal

Spent Nuclear Fuel

SNF Storage

Fuel Fabrication

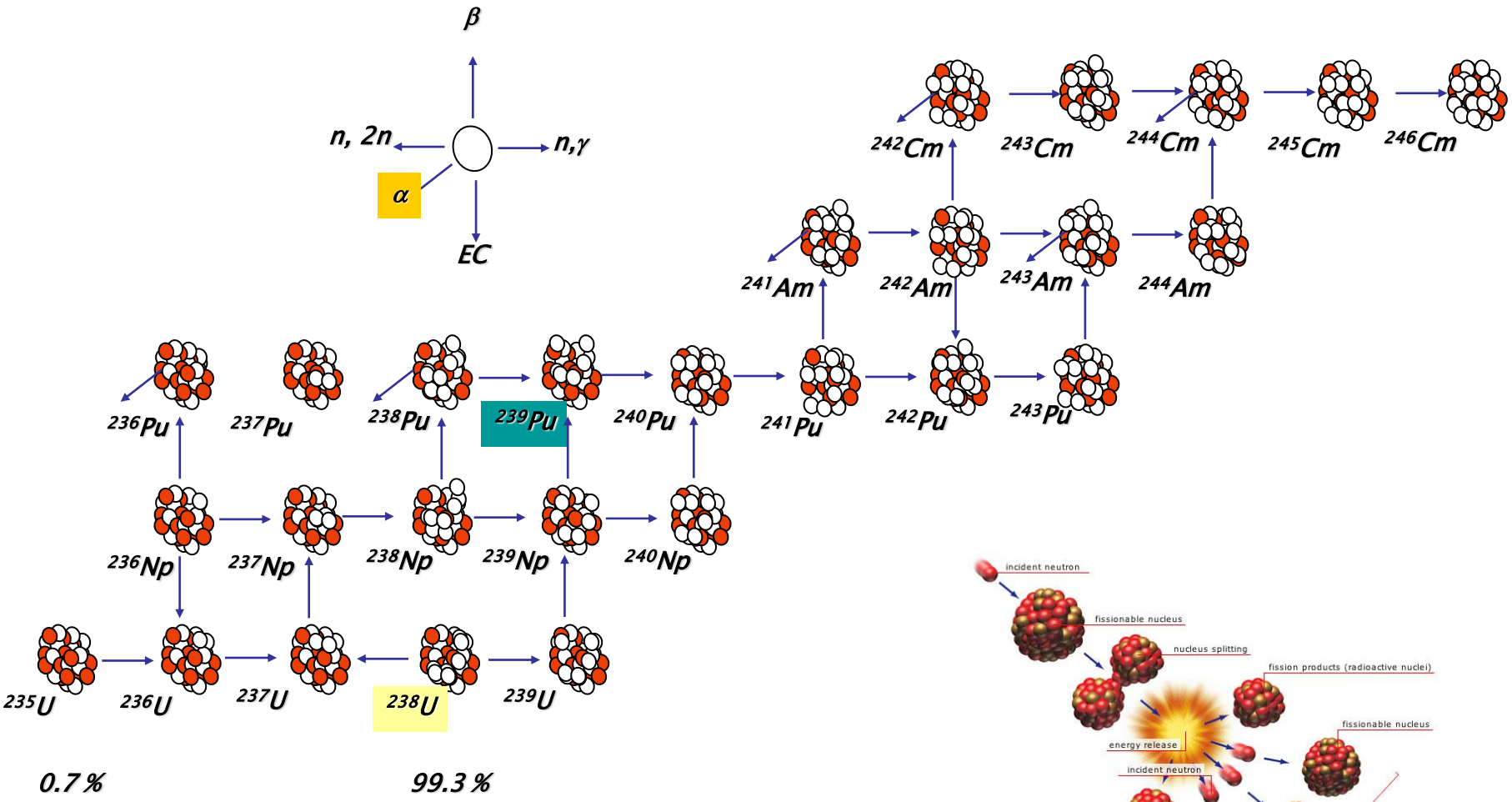
Reactor

spent fuel storage

nuclear fuels

nuclear reactor

Source of Pu and minor actinides (MA) – activation process of the fuel (neutron capture)



fission

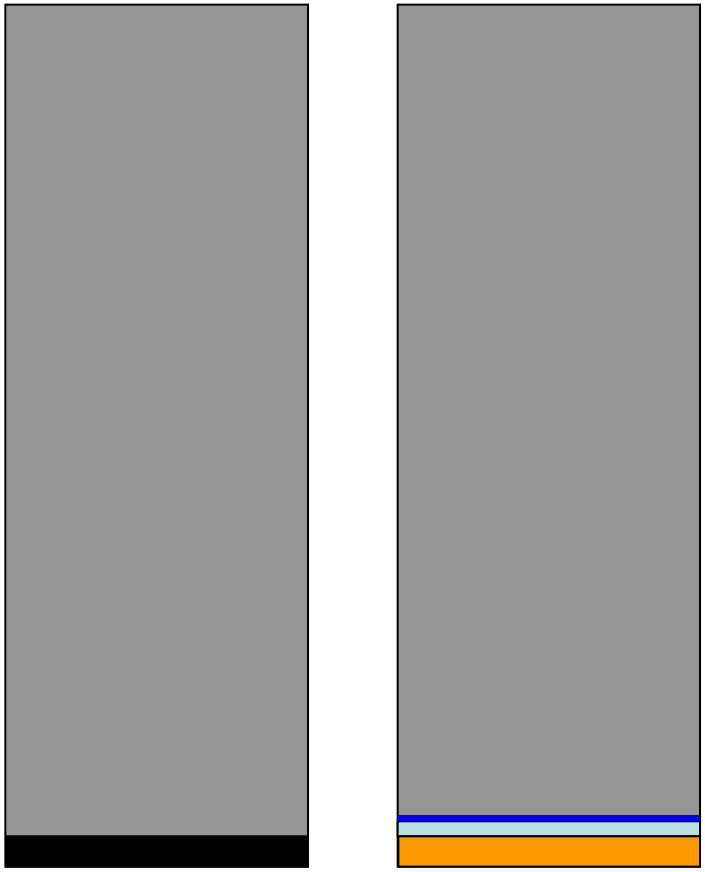
Fresh fuel *vs.* spent fuel
-> "chemical revolution"

1000 kg UO_2

↓

965 kg $^{238}UO_2$

35 kg $^{235}UO_2$



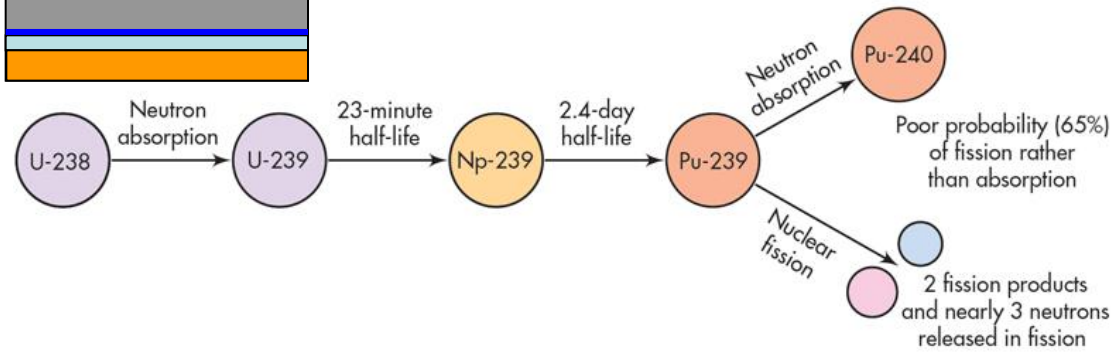
937.5 kg UO_2 (0.84% ^{235}U)

49.4 kg fission products

11.8 kg plutonium

1.3 kg minor actinides (Np, Am, Cm)

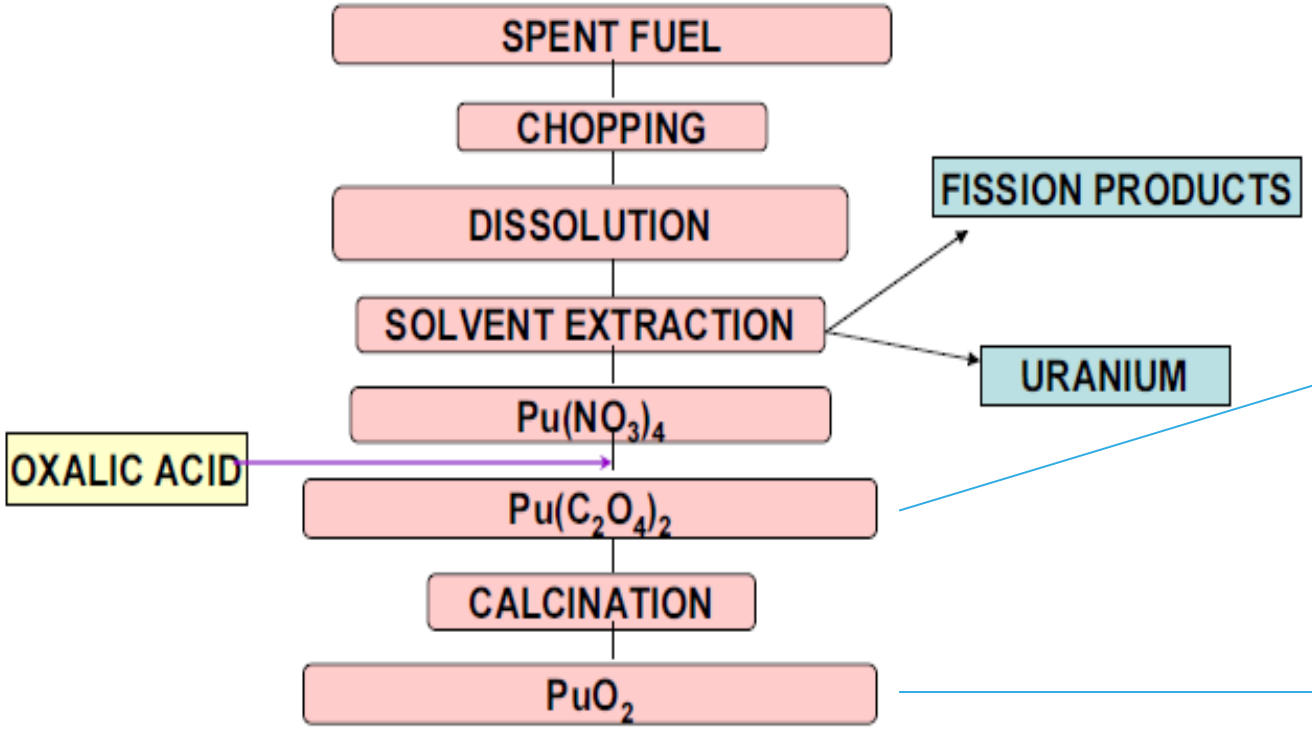
(47.5 MWd/kgU)

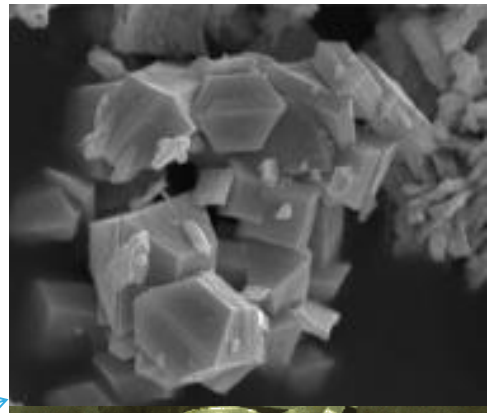


Plutonium chemistry

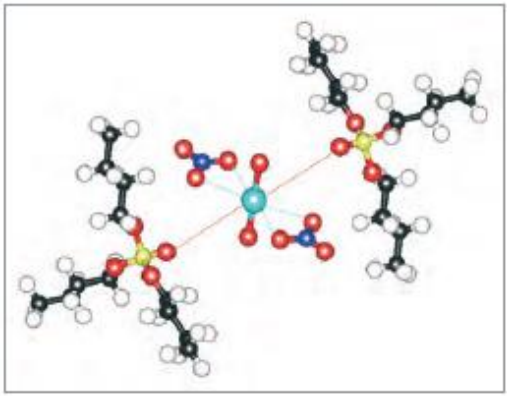
Plutonium presents different oxidation states in aqueous solution. Pu(IV) can be stabilised in 4M HNO_3.

Pu(IV) is precipitated as oxalate and thermally decomposed to submicrometric PuO_2.





Reprocessing of spent nuclear fuel (PUREX)



Recovering and Purifying

URANIUM

PLUTONIUM

SPENT FUEL

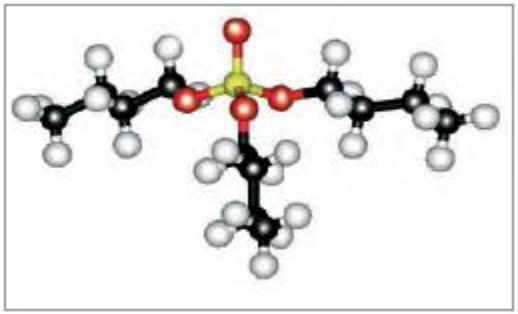
PUREX

SAFETY

RELIABILITY

FLEXIBILITY

COSTS



TBP

WASTE

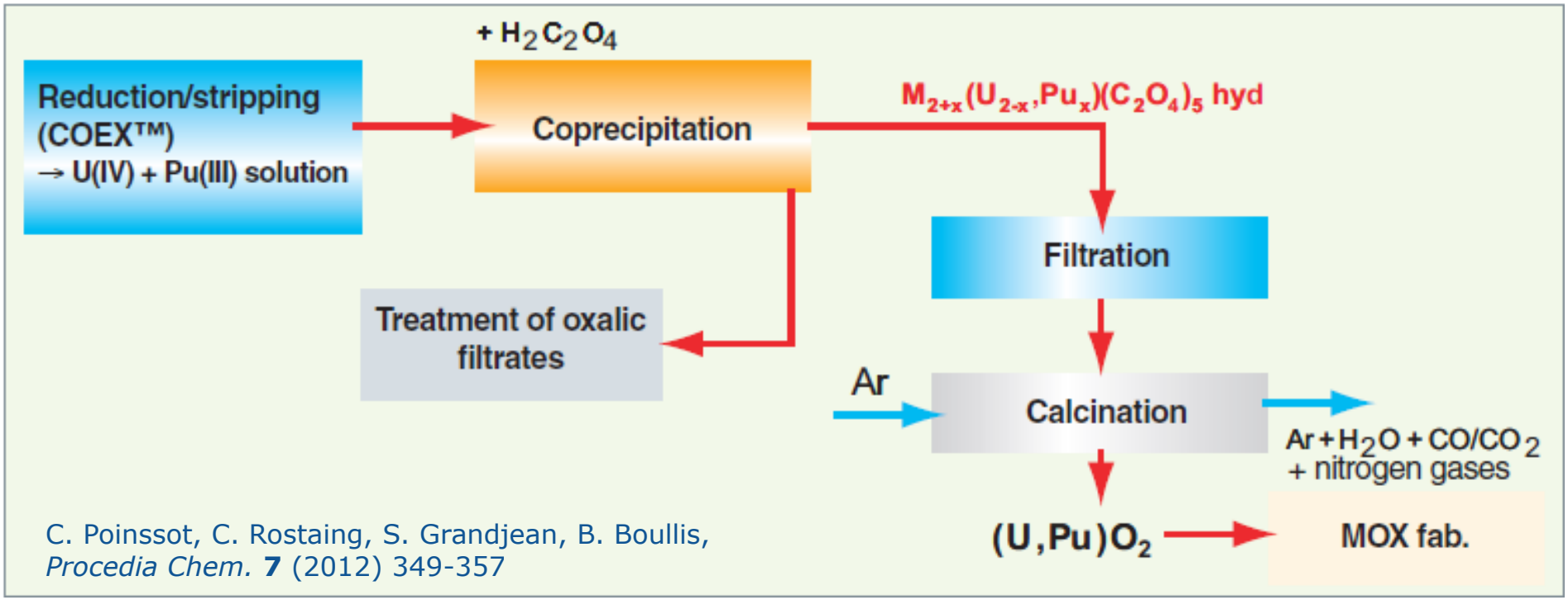
Confining and Concentrating

European Commission

Reprocessing of spent nuclear fuel (COEX)

COEX™ process evolved from PUREX process, to produce a U + Pu mixture (U/Pu > 20%),

- to curb proliferation risks
- perfectly homogeneous mixed oxide for MOX fuel fabrication with enhanced performance.



C. Poinssot, C. Rostaing, S. Grandjean, B. Boullis, *Procedia Chem.* **7** (2012) 349-357

Co-precipitation methods

Parameters to be controlled for co-precipitation:

- feed solution concentration adjustment
- precipitant concentration and addition methods
- pH, temperature, mixing method and time
- valence adjustment
- solid precipitation separation from the filtrate mother liqueur
- temperature and time for drying, calcination and reduction of powder

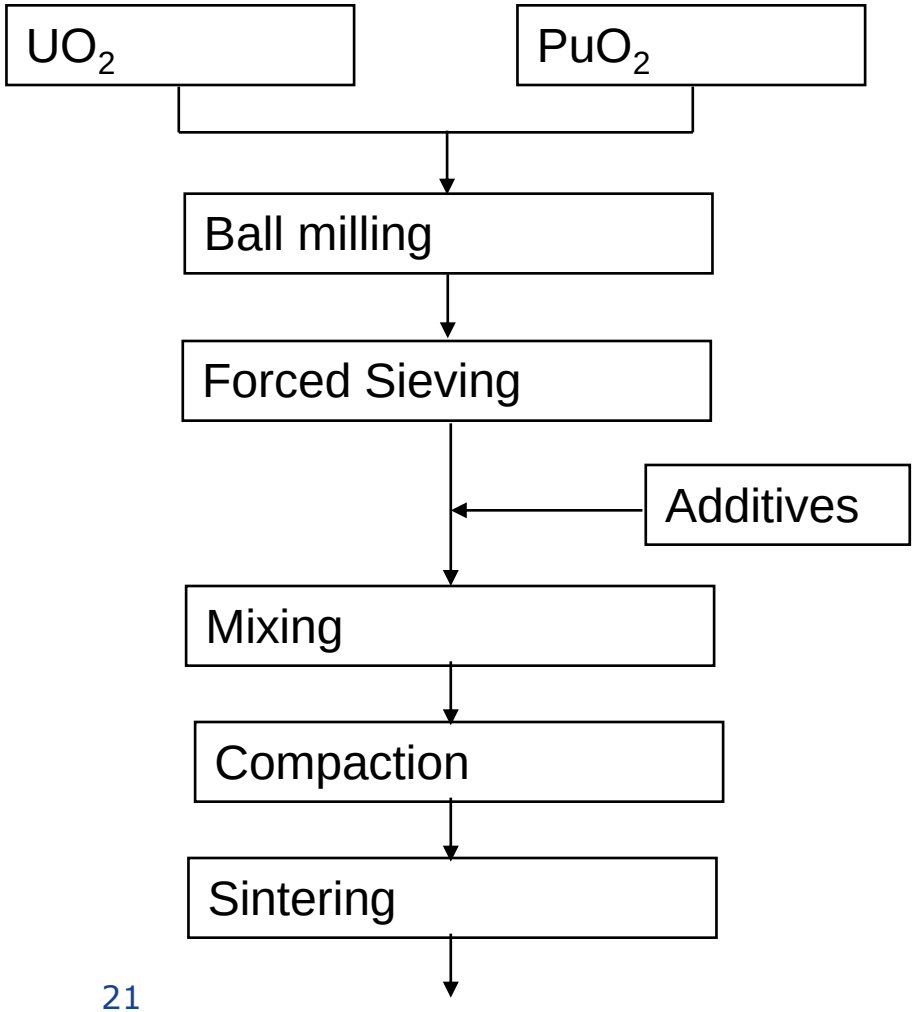
The **3 coprecipitation processes** considered for evaluation are:

- ✓ **ammonia** coprecipitation (Russia)
- ✓ **oxalate** coprecipitation (France)
- ✓ **ammonium-uranyl-plutonyl-carbonate**, AUPuC (Germany)

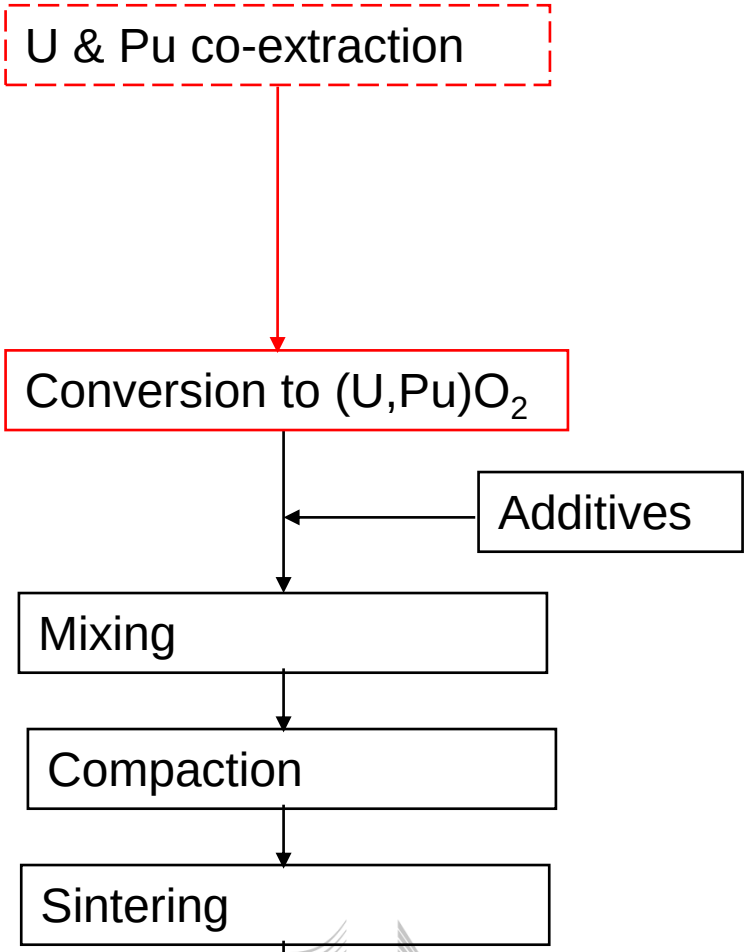
+ other **direct denitration** processes

Mixed oxide fuel fabrication methods

traditional



co-extraction



Advanced fabrication processes for ceramic nuclear fuels

- ✓ Oxalate decomposition under hot compressed water process *(oxides)*
- ✓ Citrate gel process *(carbides)*
- ✓ Molecular approach: from MOF to carbides *(carbides)*
- ✓ Sol-gel based processes for fuel manufacturing *(oxides, carbides, nitrides)*
  - vibro-sol (sphere-pac)
  - sol-gel microsphere pelletisation

Decomposition of oxalates under hot compressed water

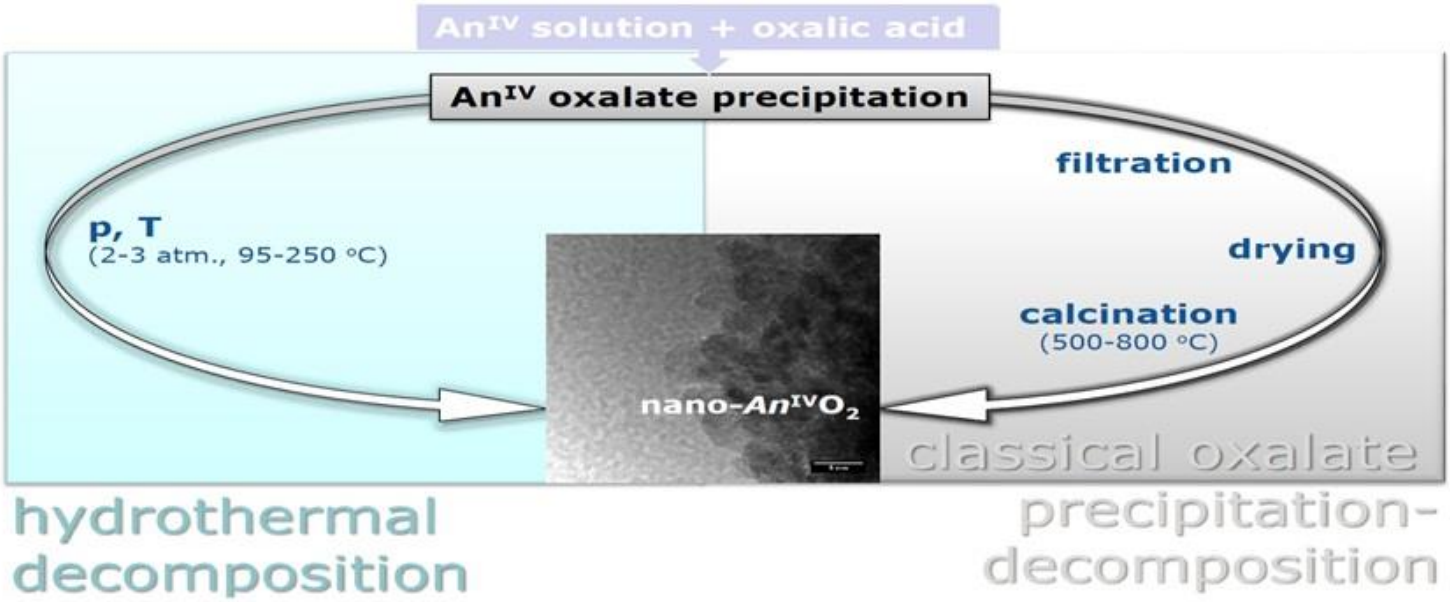
The dry oxalate decomposition:

J.F. Facer, Jr., K.M. Harmon, Precipitation of Pu(IV) oxalate, HW-31186, 1954.

A. Porter and A. E. Symonds, Precipitation of plutonium(III) oxalate and calcination to plutonium dioxide, DP-981, 1965.

The wet oxalate decomposition:

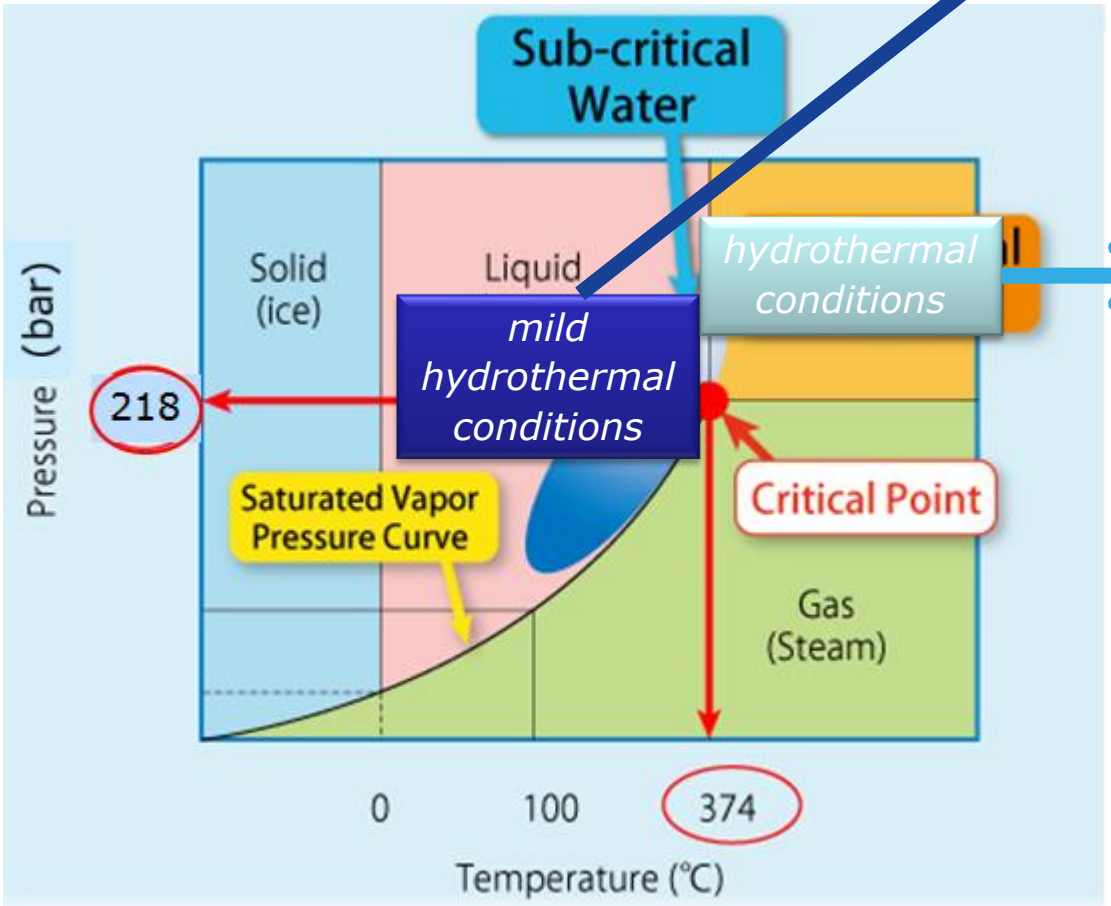
O. Walter, K. Popa, O. Dieste Blanco, Hydrothermal decomposition of actinide(IV) oxalates: a new aqueous route towards reactive actinide oxide nanocrystals, *Open Chem.* **14** (2016) 170–174.



AnO_2 and s.s. production under HCW

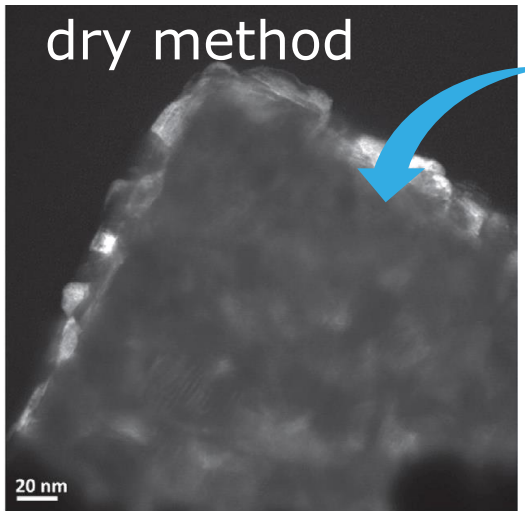
Hot compressed water (HCW): here pressured water > 95 °C

- below the thermodynamic critical point (liquid):
  mild hydrothermal conditions
- water above the thermodynamic critical point (supercritical water, SCW):
  hydrothermal conditions

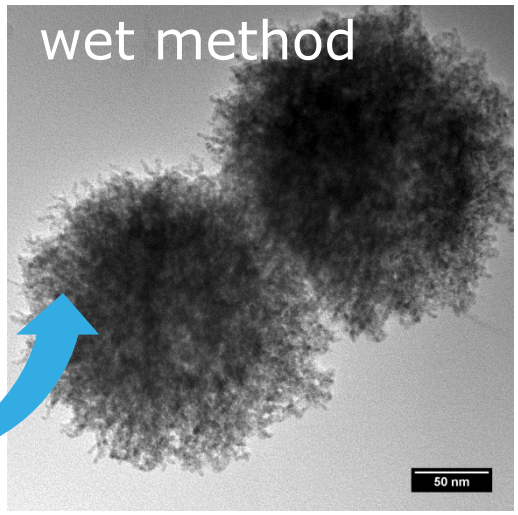


Dry/wet decomposition of An^{IV} oxalates

$An(NO_3)_4 + 2\ H_2C_2O_4 + nH_2O \rightarrow An(C_2O_4)_2{\cdot}nH_2O \rightarrow AnO_2$



U-oxalate

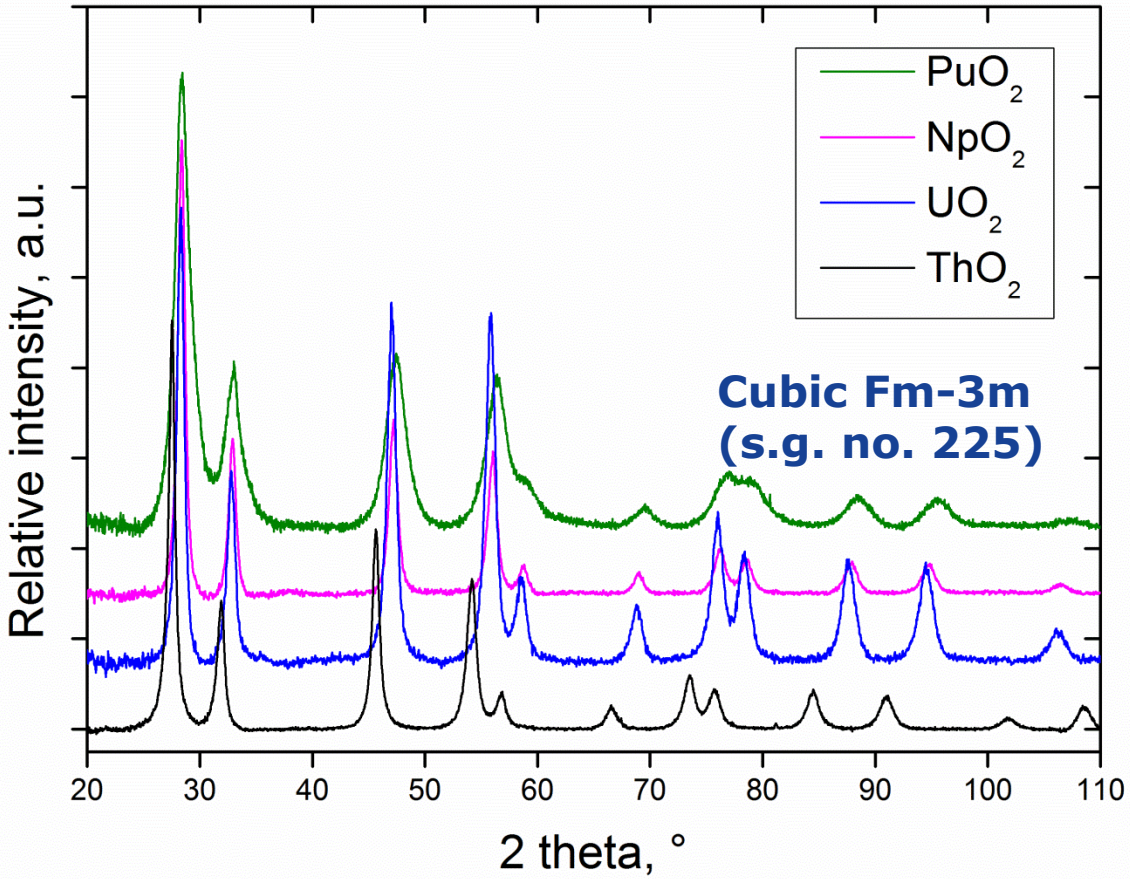


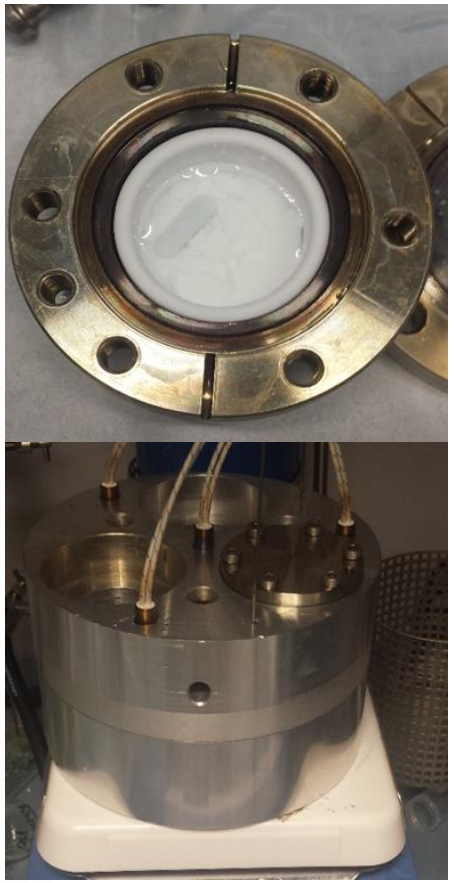
UO_2 600 °C

$UO_{2(+x)}$ 170 °C

+ low temperature
+ small nanocrystals
+ simple and versatile
+ close to quantitative
+ scale-up possible
- powders difficult to sinter

++ even lower temperature
++ even smaller NC's
+ simple and versatile
+ close to quantitative
+ scale-up possible
+ sinterable powders

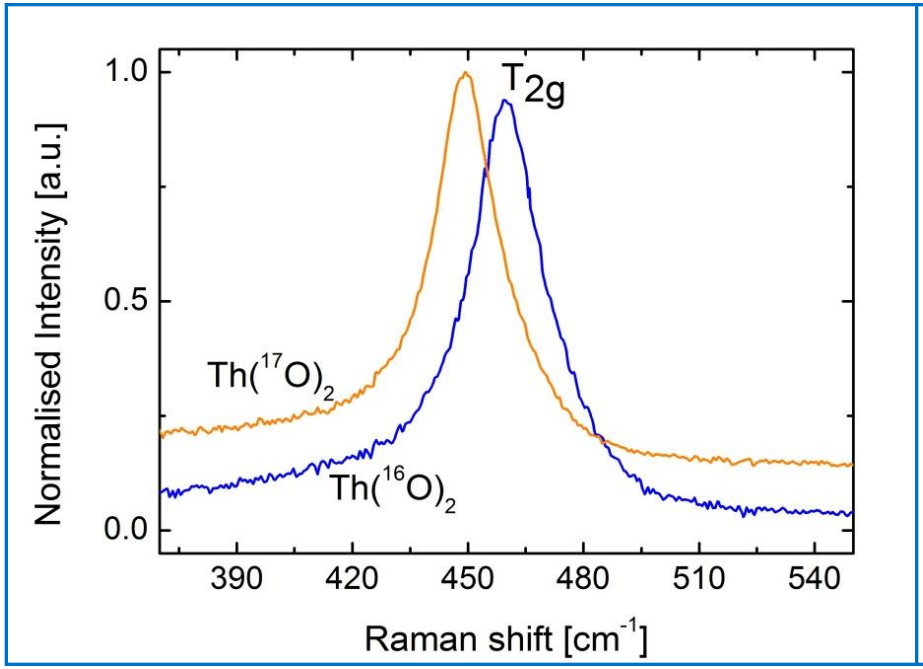


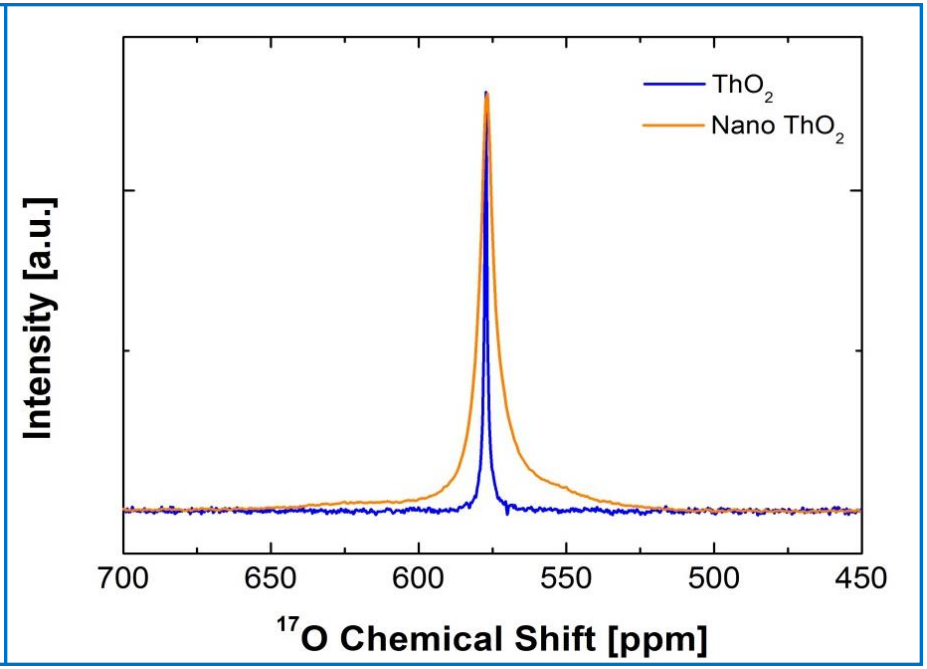


Oxide	Colour	Reaction conditions	Lattice parameter, Å	Particle size from XRD, nm
ThO_2	white	4-24 h, 250-300 °C	5.604-5.610	5-7
$UO_{2(+x)}$	black	30 min - 24 h, 160-300 °C	5.455-5.470	5-13
NpO_2	beige	18 h, 170-200 °C	5.431-5.433	5-10
PuO_2	green	4 days, 95 °C	5.397	3.7(1.0)

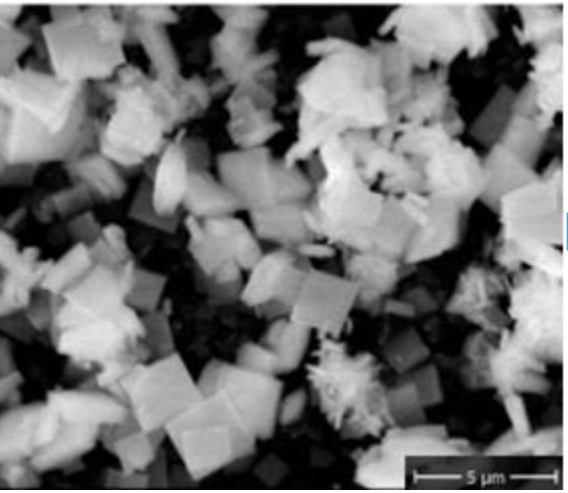
The role of the water in the hydrothermal decomposition of the oxalates

$Th(C_2{}^{16}O_4)_2{\cdot}2H_2({}^{16}O) + H_2({}^{17}O) \rightarrow Th({}^{16,17}O)_2 + 2C({}^{16,17}O) + 2C({}^{16,17}O)_2 + 3H_2({}^{16,17}O)$



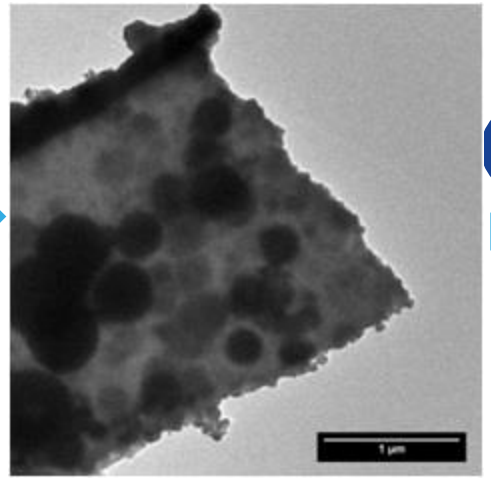


- (^{16}O) - (^{17}O) shift in the Raman spectrum
- [FWHM (T_{2g}) = 11± 2cm^{-1} → almost full substitution]
- NMR active (presence of (^{17}O) in the sample)



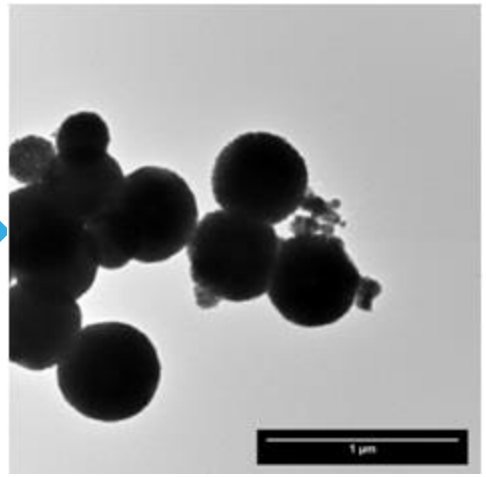
(p,T)

t_1

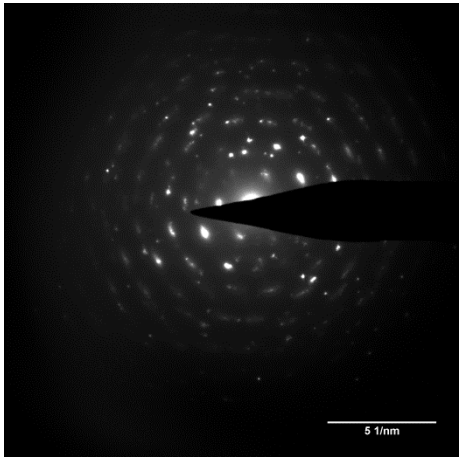


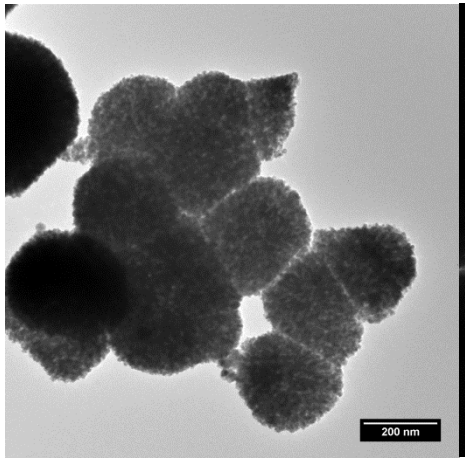
(p,T)

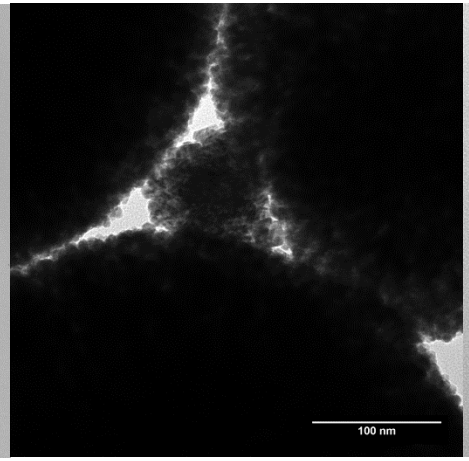
t_2

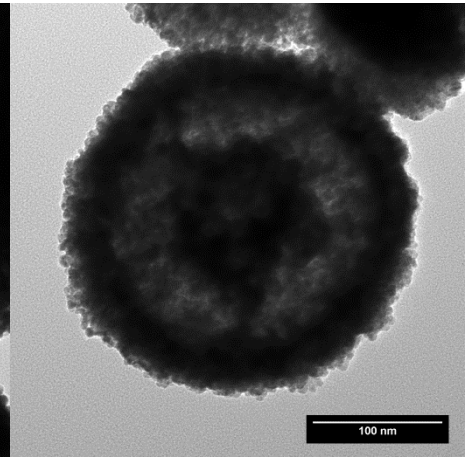


***An*-oxalate ⟶ *nc*-AnO_2**

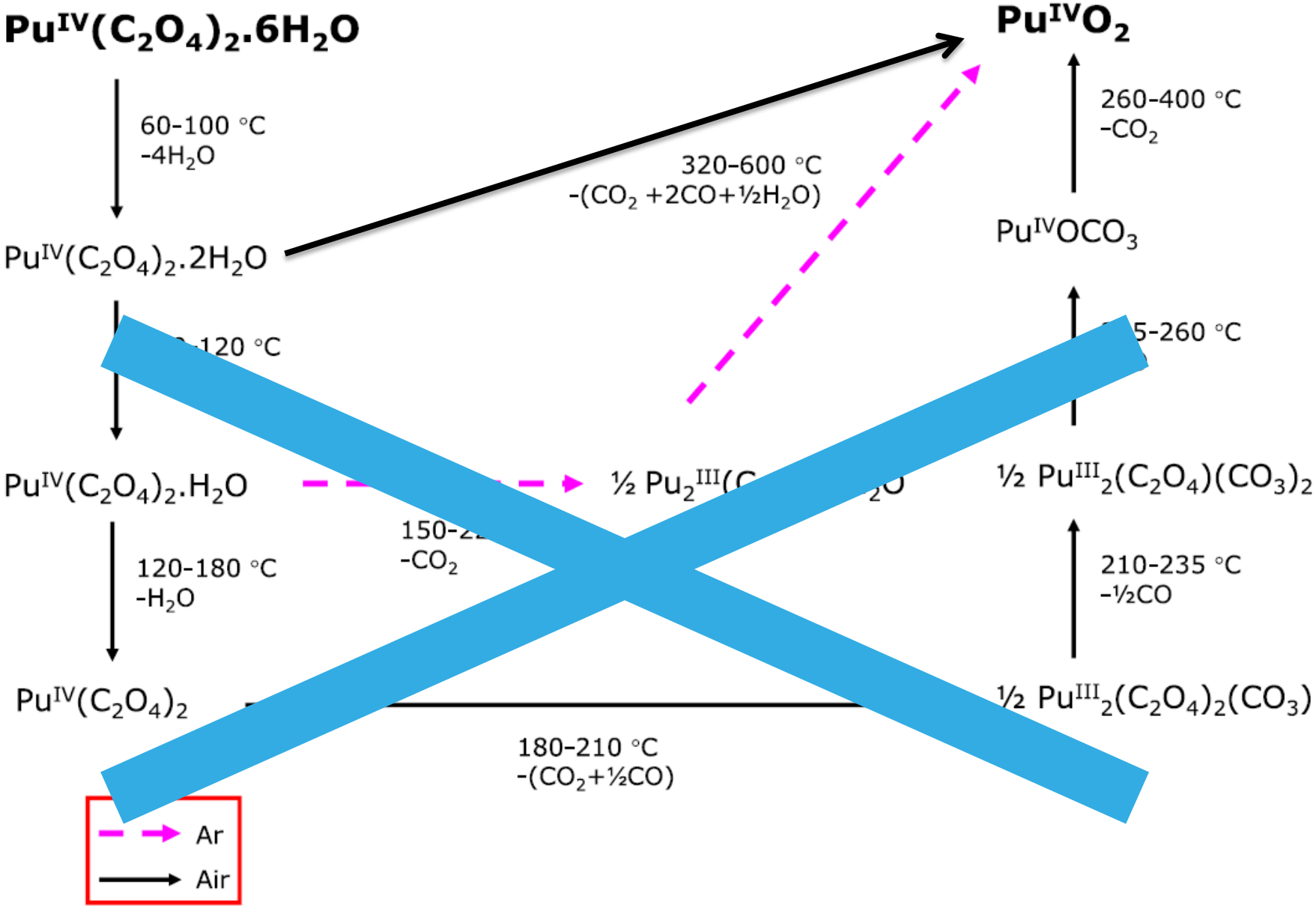








K. Popa, O. Walter, O. Dieste Blanco, A. Guiot, D. Bouëxière, L. Martel, M. Naji, J.-Y. Colle, D. Manara, "A low-temperature synthesis method for AnO_2 nanocrystals (*An*= Th, U, Np, Pu) and associate solid solutions", *CrystEngComm* **20** (2018) 4614-4622



N. Vigier, S. Grandjean, B. Arab-Chapelet, F. Abraham, "Reaction mechanisms of the thermal conversion of Pu(IV) oxalate into plutonium oxide", *J. Alloys Compd.* **444-445** (2017) 594-597

HT XRD measurements

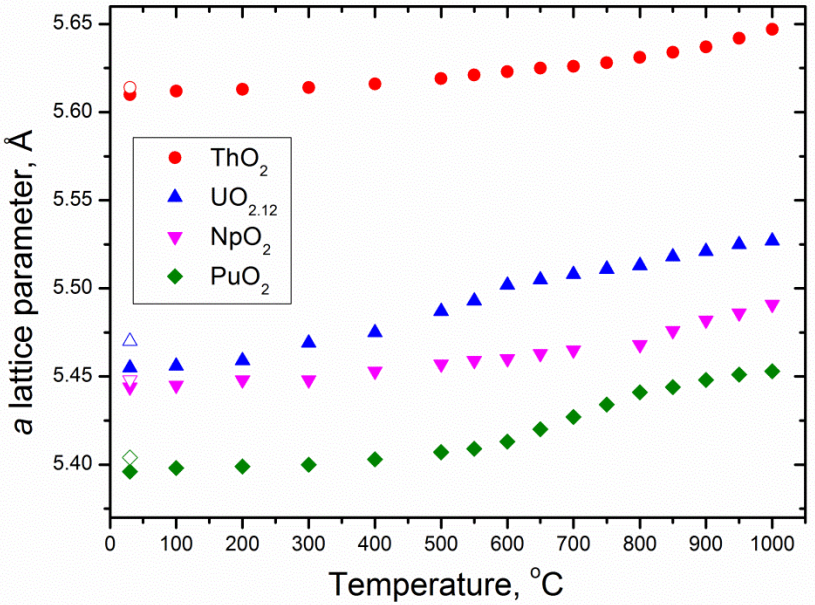
Different effects:

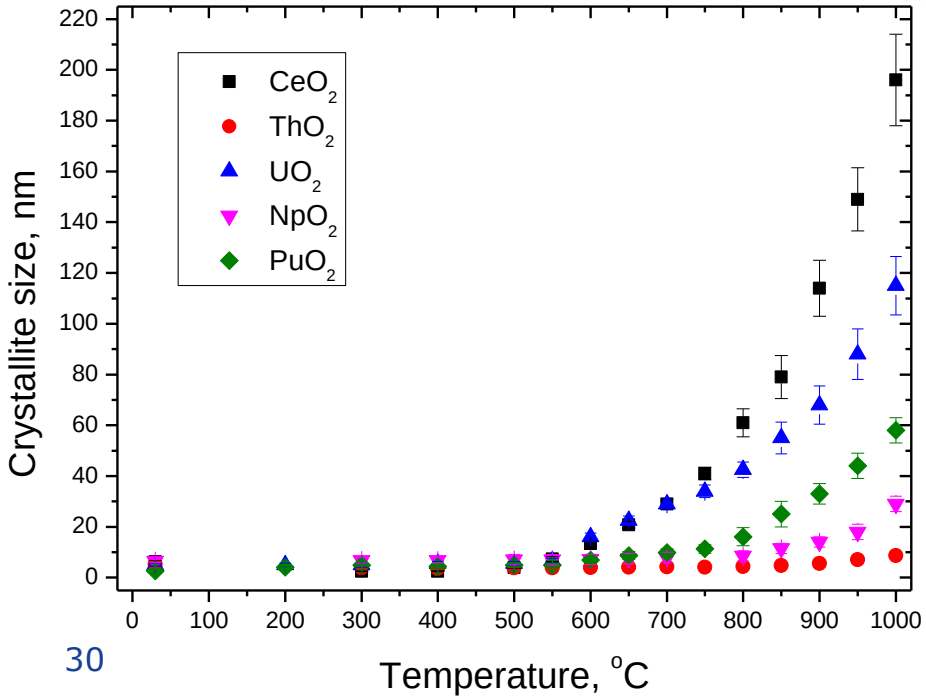
- ✓ thermal expansion
- ✓ crystallite growth
- ✓ phase transition

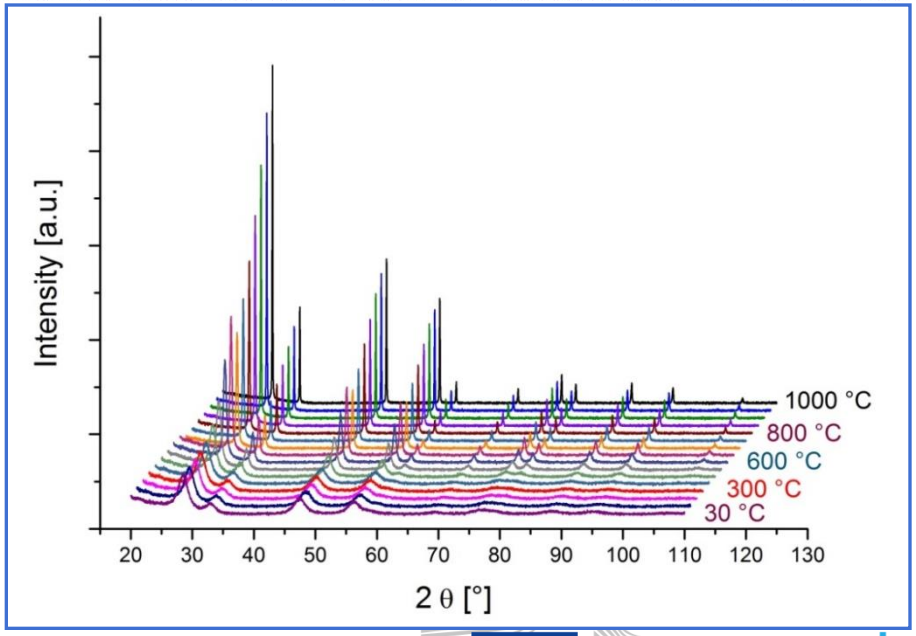
increasing T → increasing size

sintering ability:

Ce > U > Pu > Np > Th

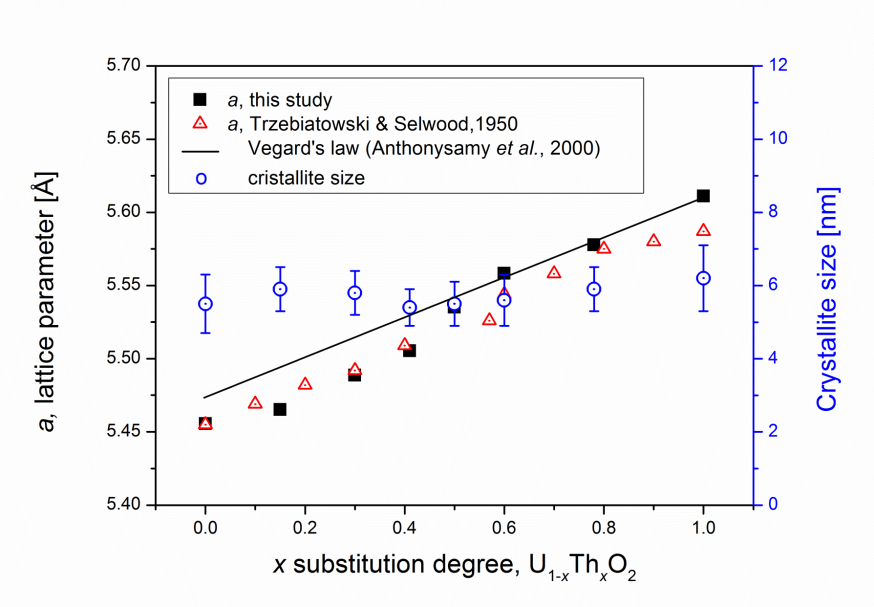


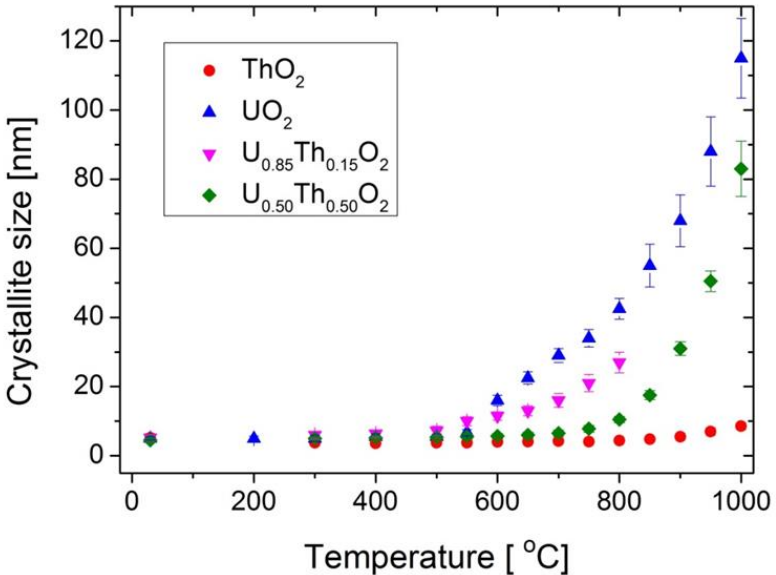


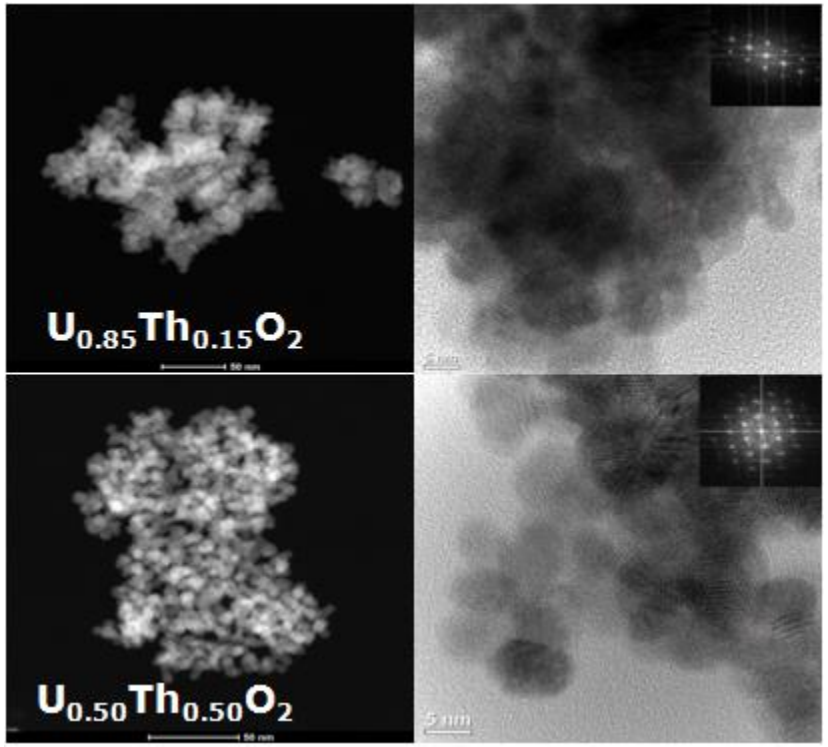


European Commission

nc-$(U,Th)O_2$ production by hydrothermal decomposition of mixed oxalates under HCW

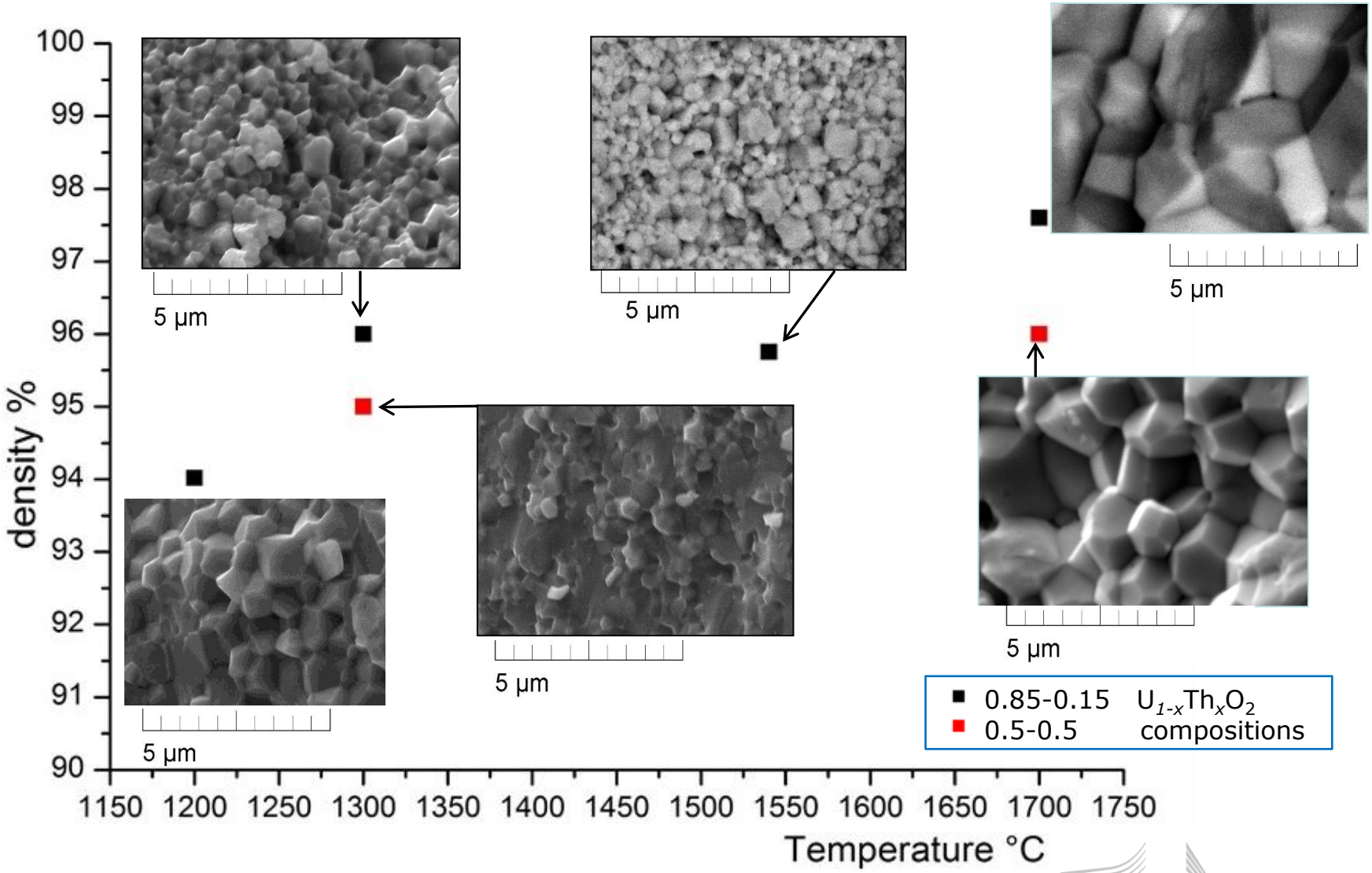






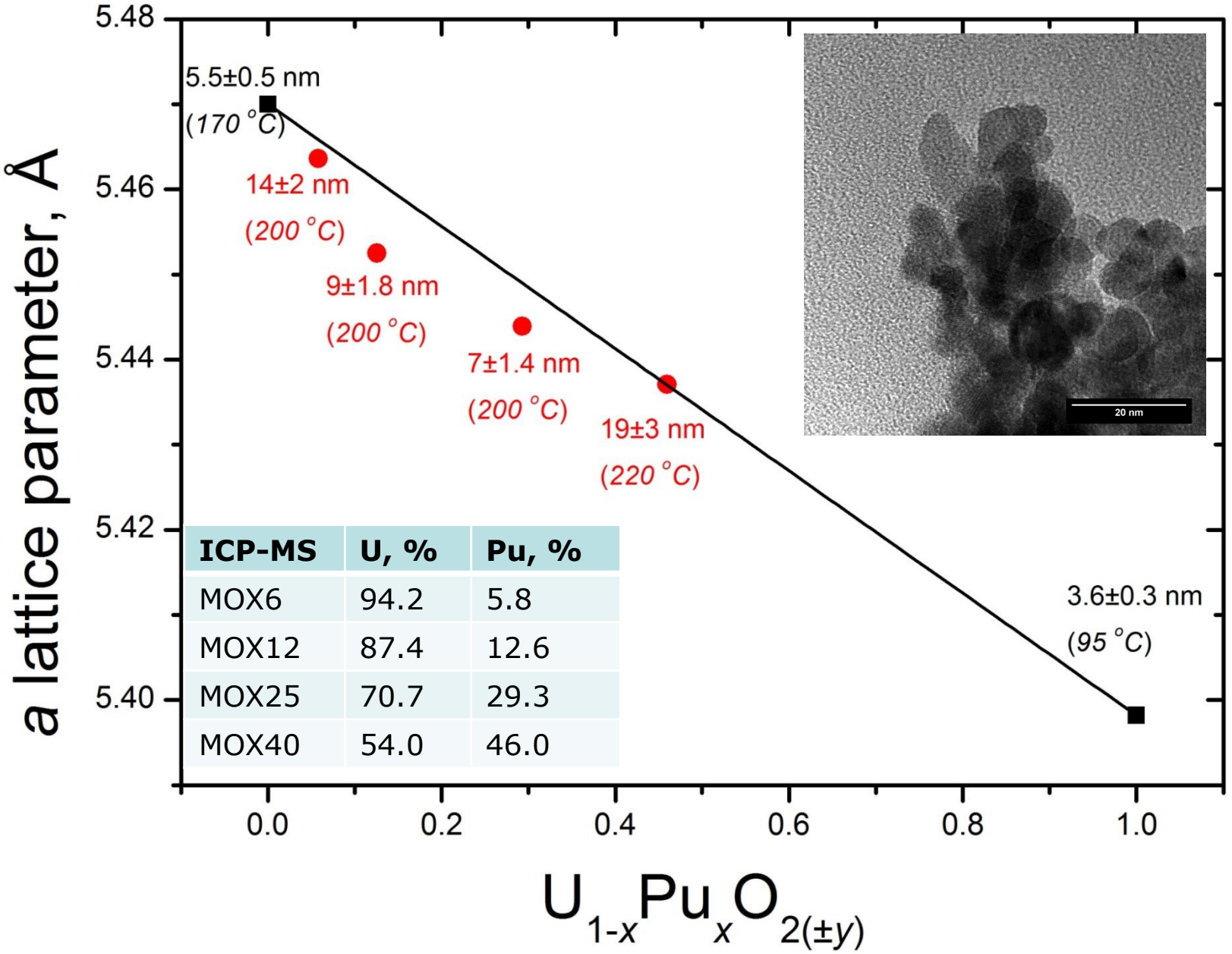
L. Balice, D. Bouëxière, M. Cologna, A. Cambriani, J.-F. Vigier, E. De Bona, D.G. Sorarù, C. Kübel, O. Walter, K. Popa, "Nano and micro $U_{1-x}Th_xO_2$ solid solutions: from powders to pellets", *J. Nucl. Mater.* **498** (2018) 307-313

SPS sintering behaviour of *nc*-$U_{1-x}Th_xO_2$ *(Masters Luca Balice)*



European Commission

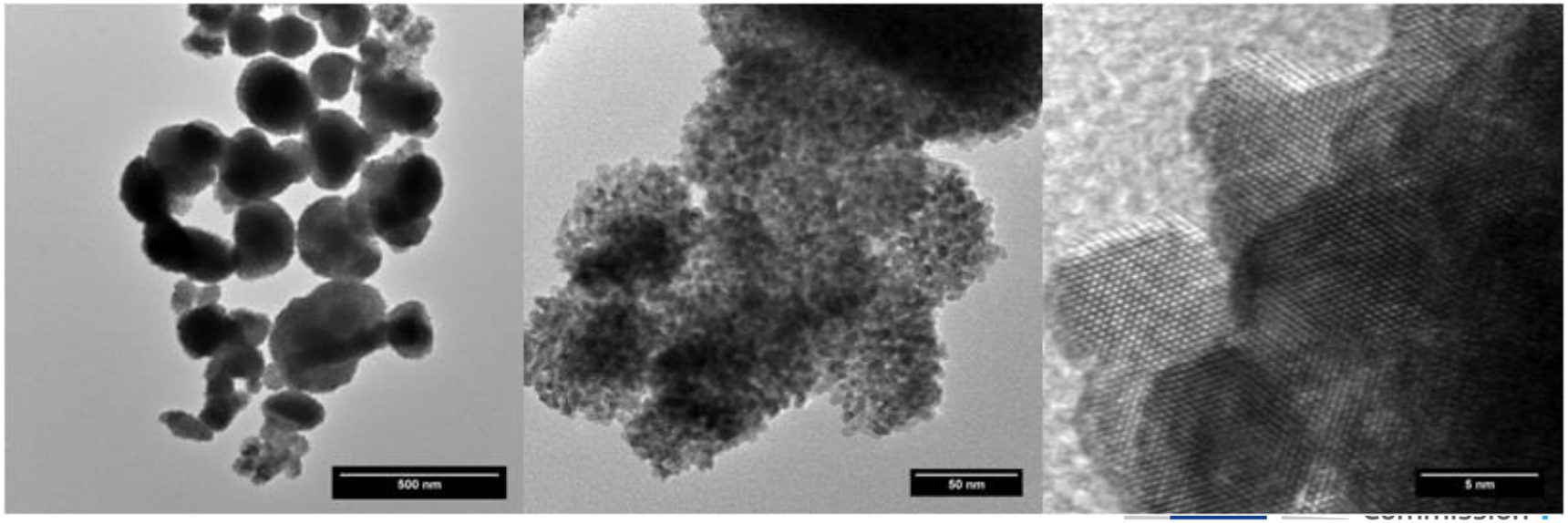
nc-$(U,Pu)O_{2(\pm y)}$ production *(PhD Guilhem Kauric)*

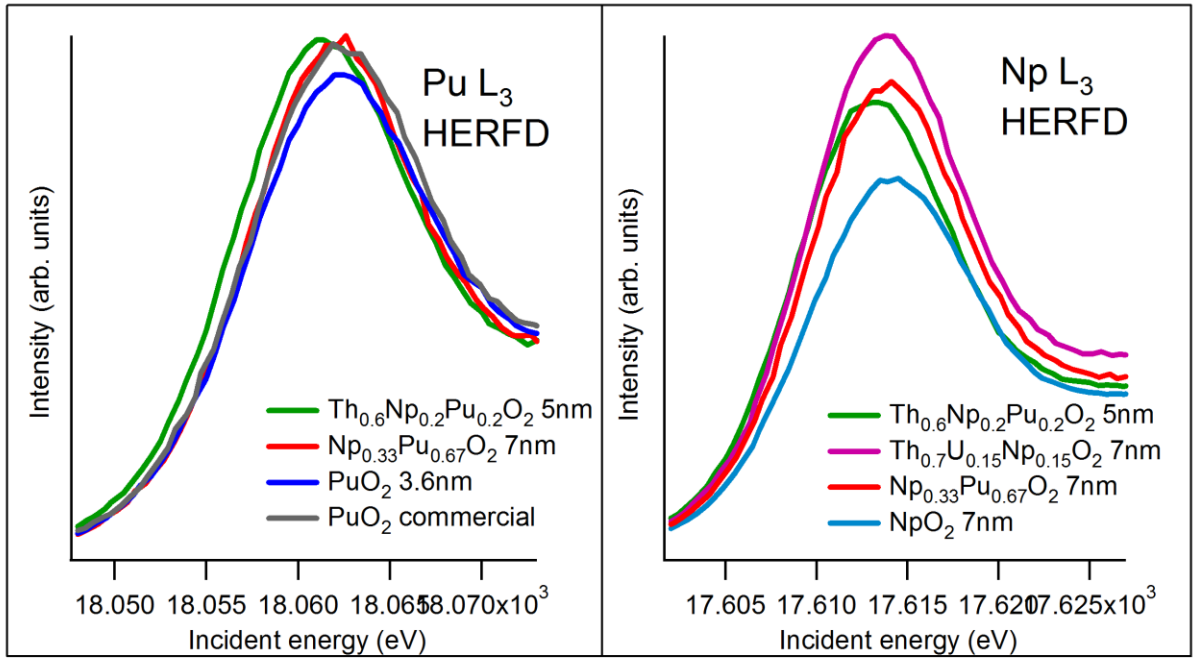


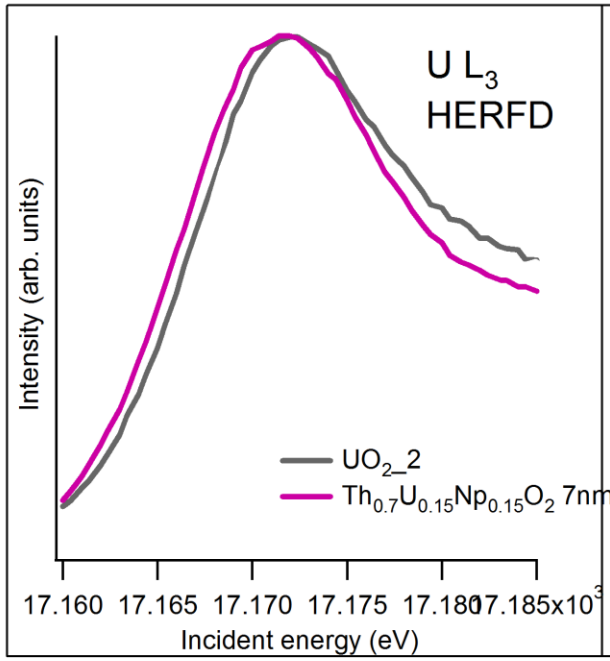
ICP-MS	U, %	Pu, %
MOX6	94.2	5.8
MOX12	87.4	12.6
MOX25	70.7	29.3
MOX40	54.0	46.0

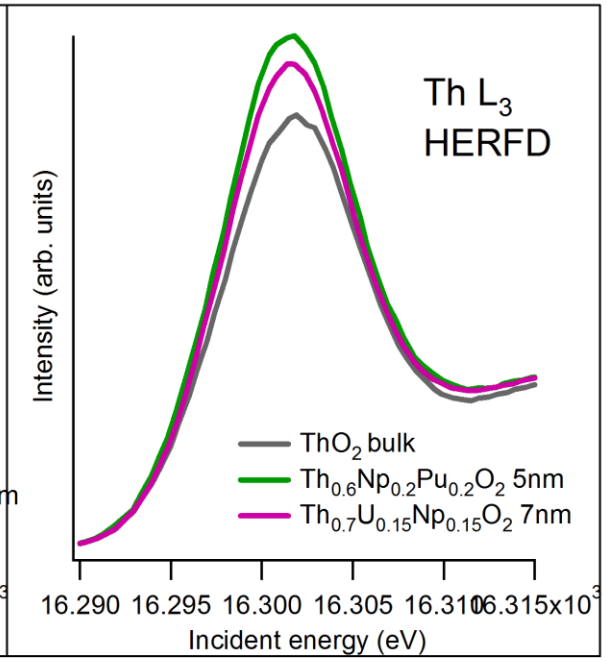
Multicomponent mixed oxides production by hydrothermal decomposition of oxalates under HCW

Composition	Reaction conditions	a, Å	d, nm	Colour
$Th_{0.70}U_{0.15}Np_{0.15}O_2$	18 h/ 200 °C	5.530	7.0 ± 2.5 (XRD)	brown
$Th_{0.45}U_{0.10}Pu_{0.45}O_2$	18 h/ 200 °C	5.450 5.522	8.5 ± 2.0 (XRD) 6.2 ± 1.1 (TEM)	grey
$Th_{0.80}Pu_{0.20}O_2$	18 h/ 200 °C	5.510 5.583	6.8 ± 0.9 (XRD) 4.1 ± 0.5 (TEM)	pale green
$Np_{0.33}Pu_{0.67}O_2$	18 h/ 200 °C	5.411	8.4 ± 1.6 (XRD)	light grey
$Th_{0.60}Np_{0.20}Pu_{0.20}O_2$	18 h/ 200 °C	5.520	5.0 ± 1.1 (XRD)	light green







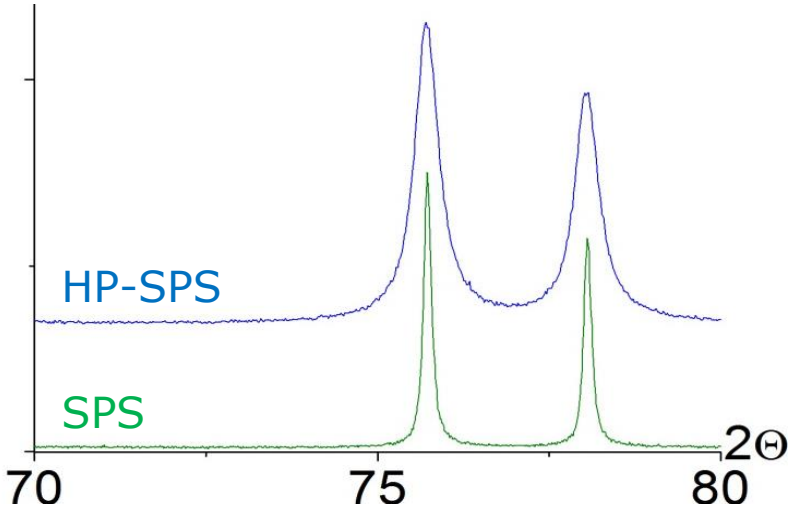


An oxidation state

K. Kvashnina,
K. Popa, O. Walter
unpublished results

European Commission

Separate effect study *(PhD Emanuele de Bona)*



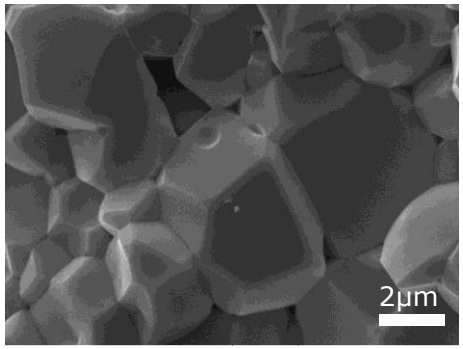
95% TD (geometrical density)

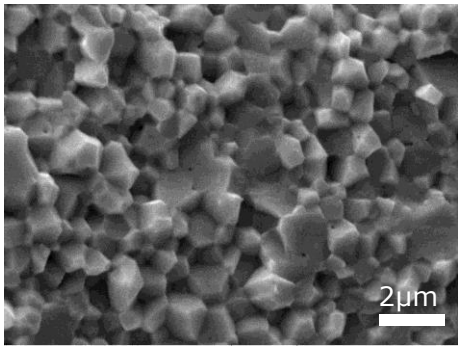
Grain size down to ~50 nm

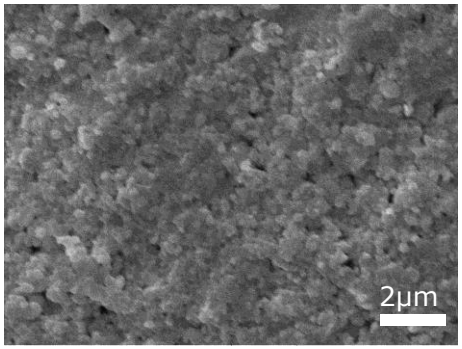
a = 5.47 Å ⟹ $UO_{2.00}$

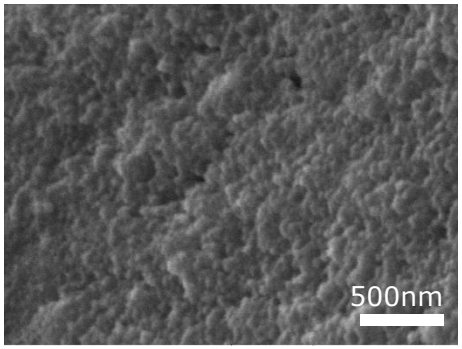
$$a = 5.4705 - 0.132x$$

350-700 °C









conventional SPS
representative of freshly sintered nuclear fuel

Two step SPS
High Burnup Structure (pore formers needed)

High pressure SPS
nanometric grains separate effect studies

European Commission

Separate effect study *(PhD Emanuele de Bona)*

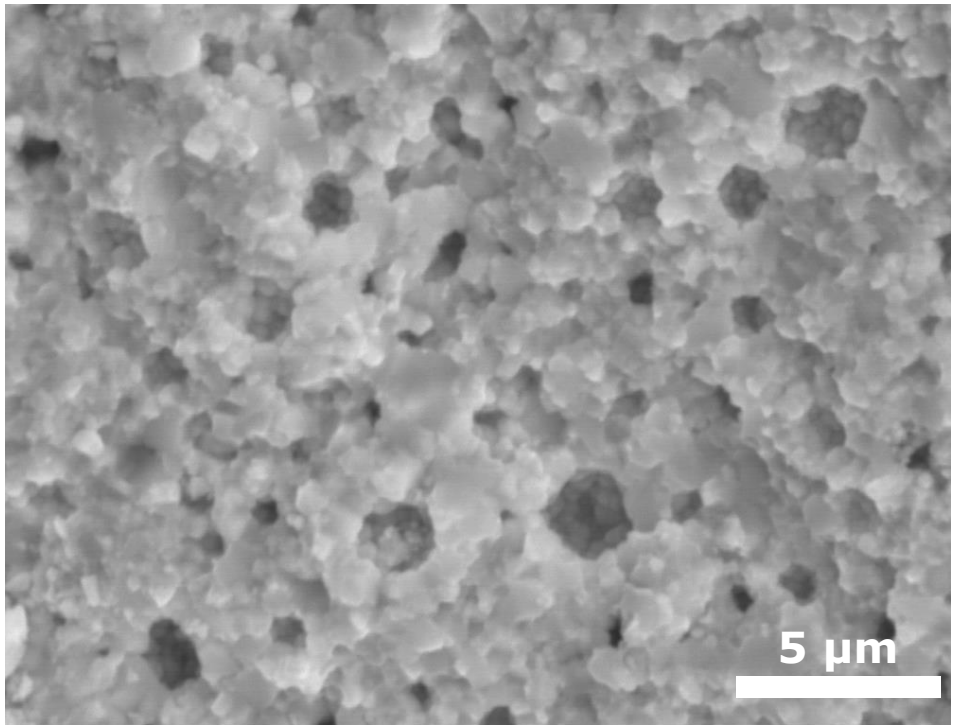
The High Burnup Structure

Microstructural reorganisation during operation:

5-10 µm grains

↓

~ 300 nm grains
+
Micrometric pores



Separate effect study

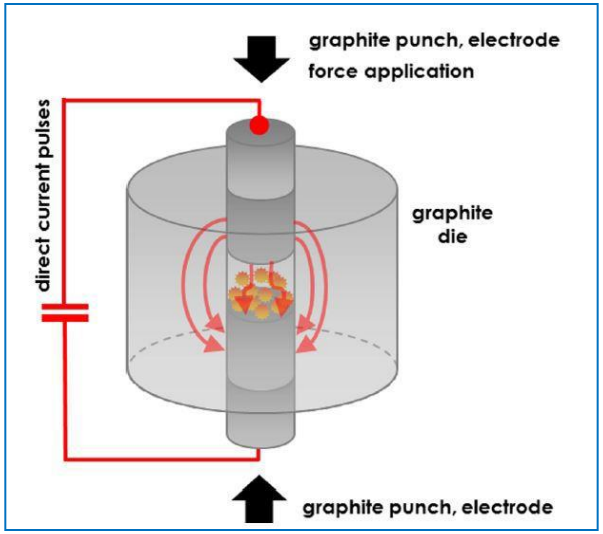
Microstructure
Porosity
Fission products
(chemical composition)

→ Thermal properties
→ Mechanical properties

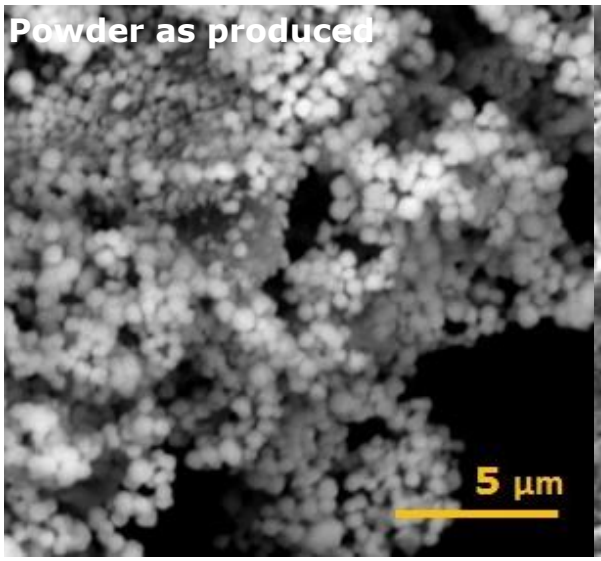
He behaviour
Rad. damage resistance
Gases retention
…

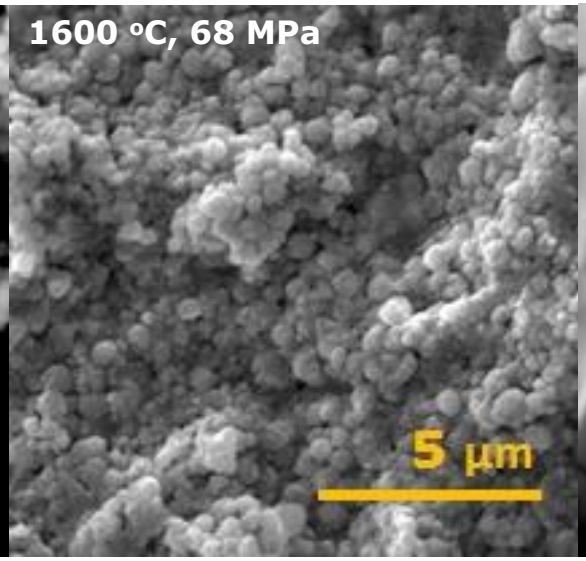
European Commission

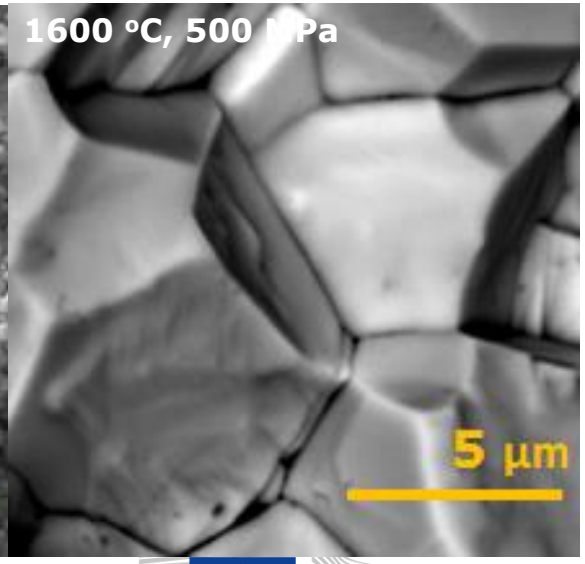
Sintering behaviour of *nc*-ThO_2 under SPS



- FAST: field assisted sintering technique
- Application of a pulsing direct current through graphite dies
- Application of pressure up to 100 MPa for graphite assembly
- consolidation into dense pellets (>90% TD) obtained at low temperatures and in a short time







Non-oxide ceramic fuels - nitrides

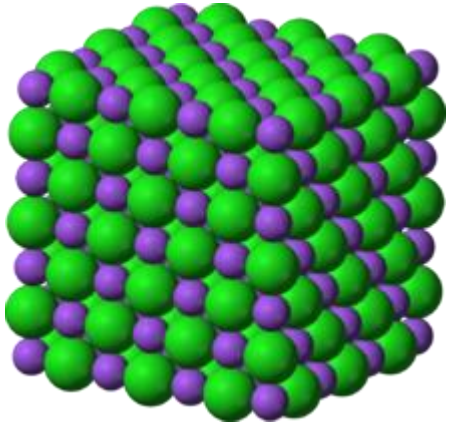
Nitride fuels refers to a family of several ceramic materials: UN, U_2N_3 and UN_2. Similar $(U,Pu)N_x$ exists

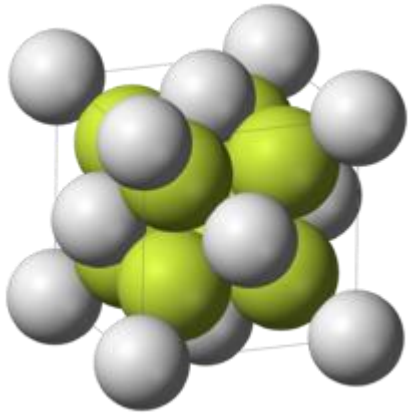
Advantages:

- ✓ safer, stronger, denser
- ✓ more thermally conductive
- ✓ higher temperature tolerance compared to oxides

Disadvantages:

- ✓ complex conversion route from enriched UF_6,
- ✓ need to prevent oxidation during manufacturing
- ✓ large amount of ^{14}C would be generated from the nitrogen by the (n,p) reaction
- ✓ need to define and license a final disposal route





Non-oxide ceramic fuels - nitrides

Carbothermic reduction

$3UO_2 + 6C \rightarrow 2UC + UO_2 + 4CO$ (Ar, 1450 °C/10 h)

$4UC + 2UO_2 + 3N_2 \rightarrow 6UN + 4CO$

Sol-gel methods

Arc melting of pure uranium under N_2 atmosphere

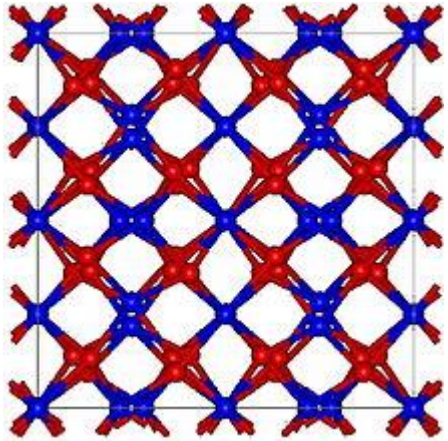
Ammonolysis UF_4 is exposed to ammonia gas under high pressure and temperature

Hydriding-nitriding

$2U + 3H_2 \rightarrow 2UH_3$ (T> 280 °C)

$2UH_3 + 1.5N_2 \rightarrow U_2N_3$ (T> 500 °C)

$U_2N_3 \rightarrow UN + 0.5N_2$ (T> 1150 °C)

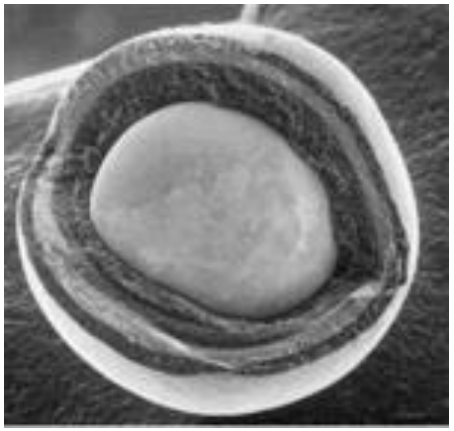


Non-oxide ceramic fuels - carbides

Carbide fuels refers to a family of several ceramic materials: UC, U_2C_3 and UC_2. Similar $(U,Pu)C_x$ exists. Also UCO and similar (U,Pu)CO are under consideration

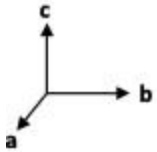
Advantages:

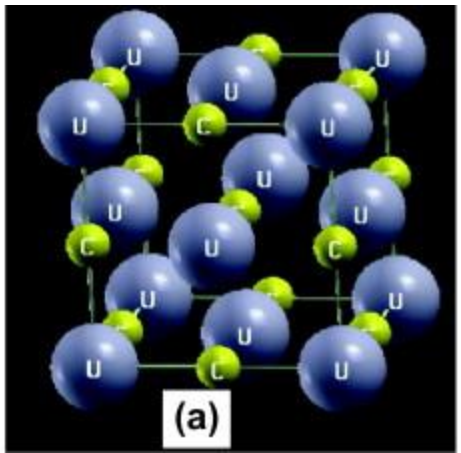
- ✓ high thermal conductivity
- ✓ high melting point
- ✓ ability to complement a ceramic coating

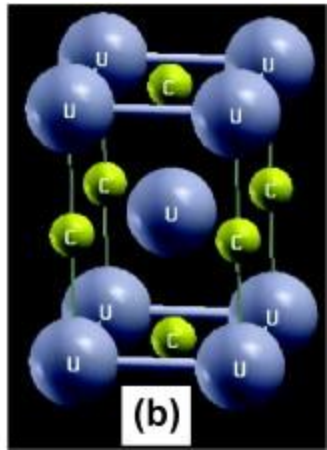


Disadvantages:

- ✓ complex production route
- ✓ burn in air atmosphere
- ✓ high production temp. (sintering)?

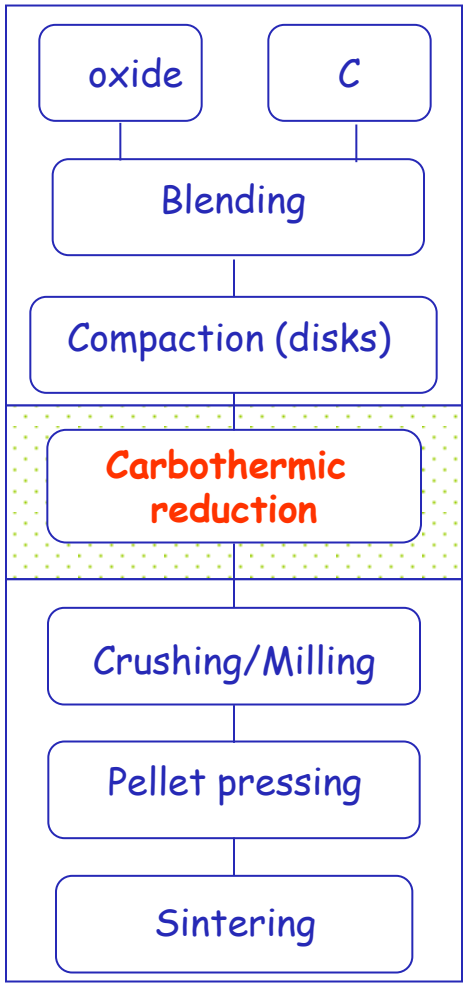




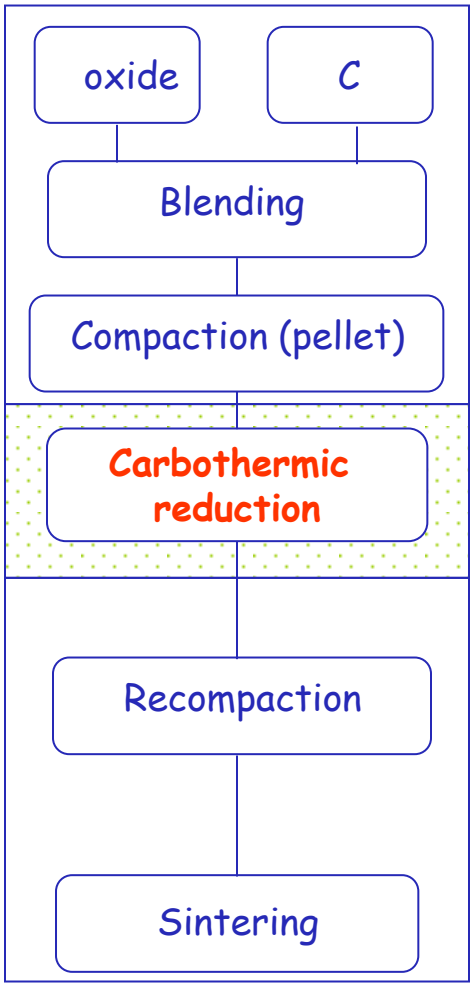


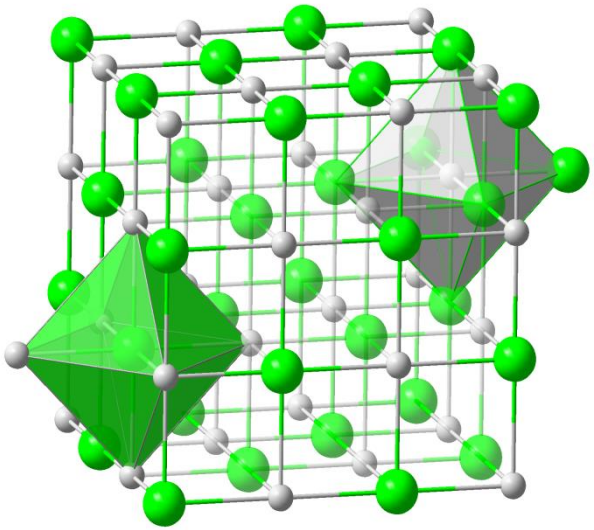
Carbides production (traditional)
Carbothermic reduction processes

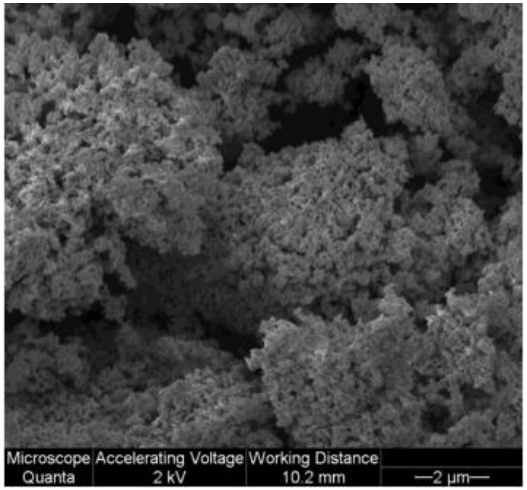
Conventional method



Direct pressing







European Commission

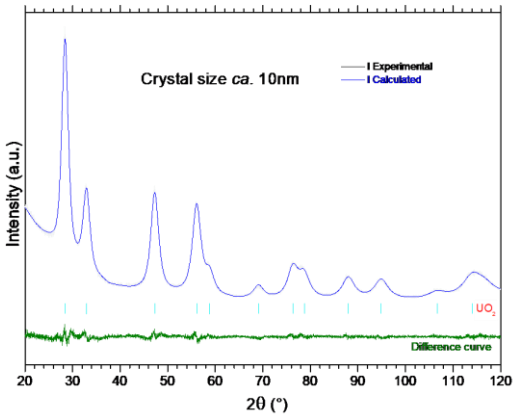
The citrate gel method *(Masters Daniele Salvato)*

$(UO_2)NO_3$ solution

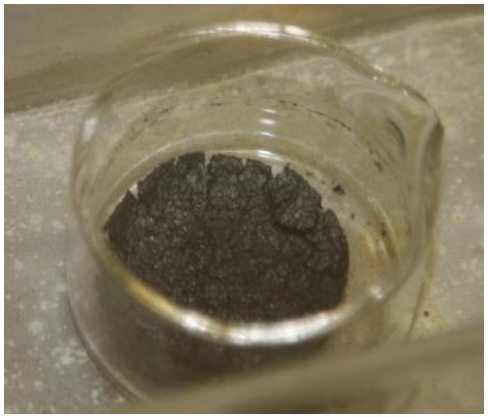
Citric acid solution

TGA

Calcination
1000 °C, 2h, Ar

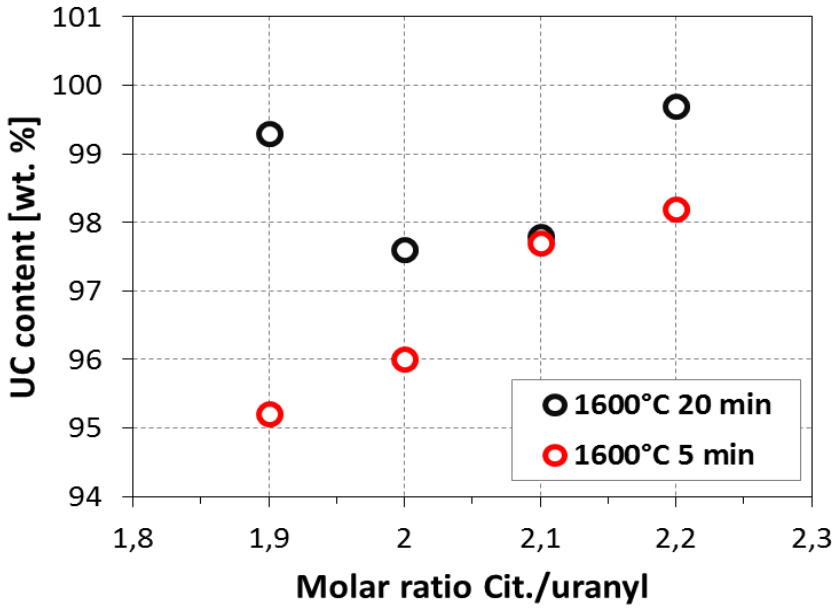


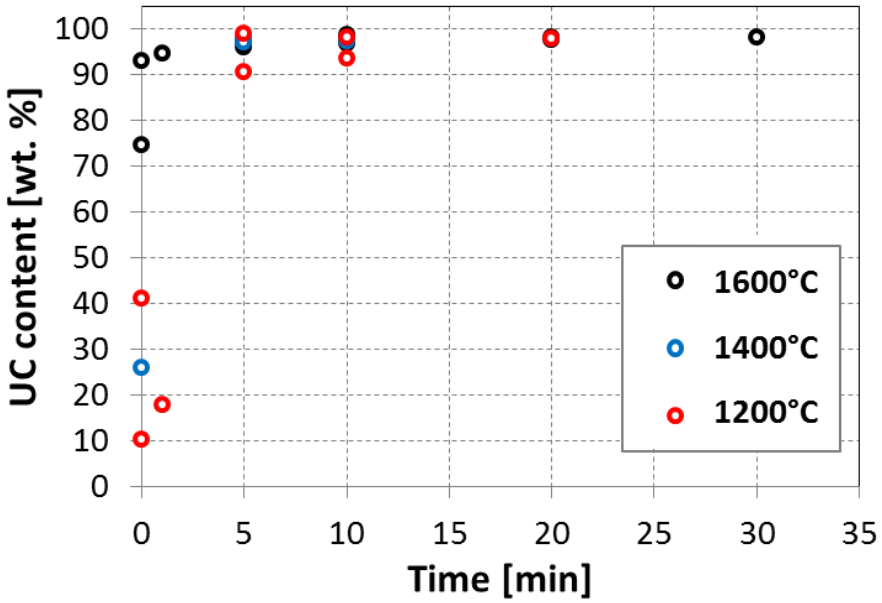
Agglomerates of UO_2 nano-crystals embedded in amorphous carbon



European Commission

The citrate gel method *(Masters Daniele Salvato)*



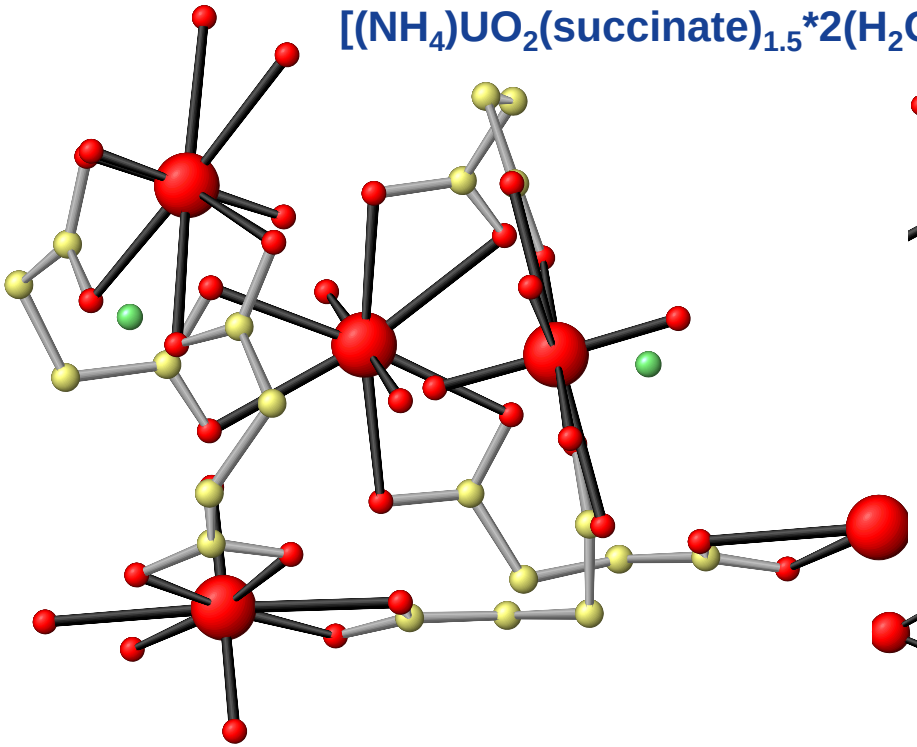


- High reactivity of the starting UO_2 + C mixture (Conventional Carbothermal reduction, 1h, Ar)
- Reactive-sintering in SPS unsuccessful (CO release problems?)
- Carbothermal Reduction in SPS allowed us to synthetize UC in few minutes << several hours conventionally needed
- High sinterability of the powder produced at low temperatures (>90%TD, in few minutes)

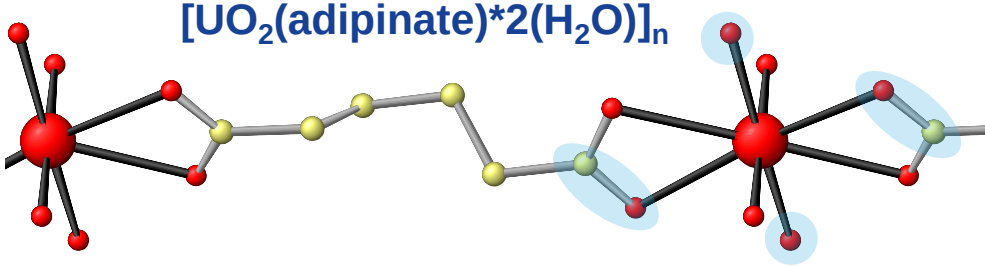
The molecular approach: from MOF to material

Synthesis of molecular precursors with a via the molecular stoichiometry well defined U to C ratio in an already described geometry (no physical mixing, no ball milling, aso)

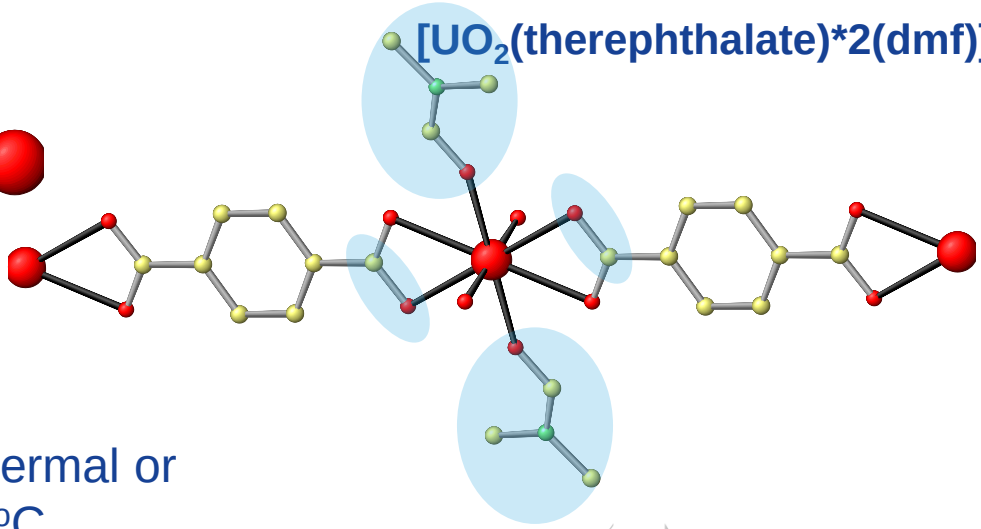
$[(NH_4)UO_2(succinate)_{1.5}*2(H_2O)]_n$



$[UO_2(adipinate)*2(H_2O)]_n$



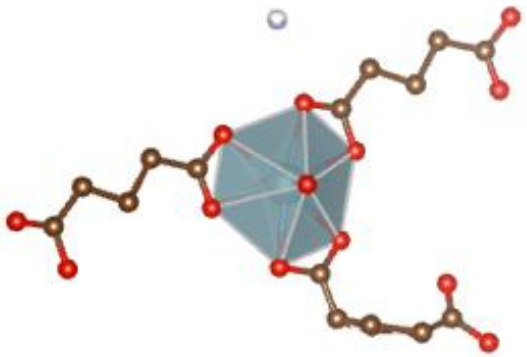
$[UO_2(therephthalate)*2(dmf)]_n$

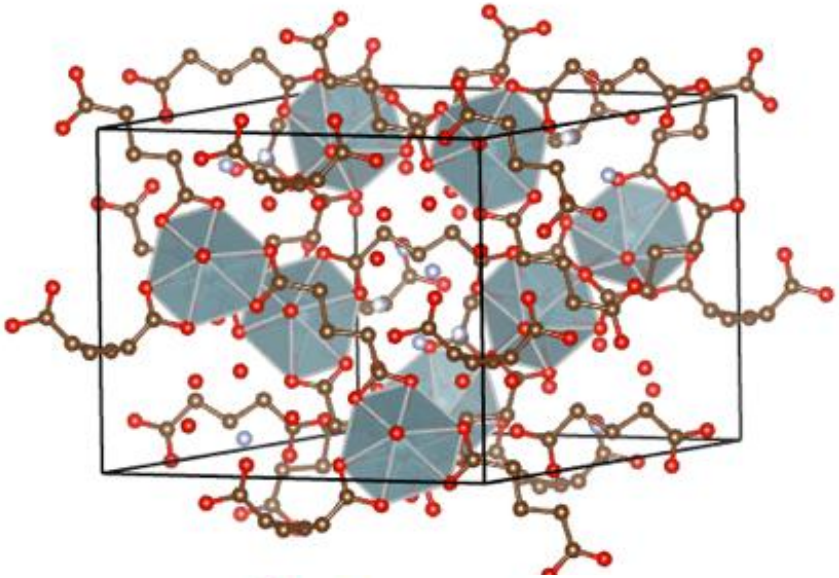


Synthesis performed under hydrothermal or solvothermal conditions, 3h at 120 ^oC

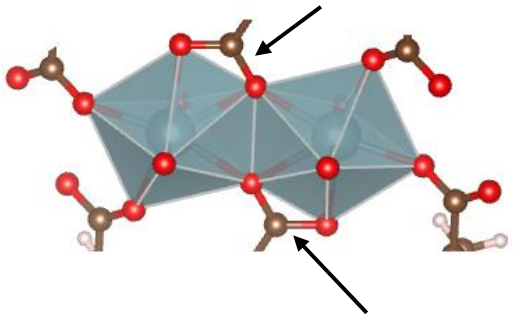
MOF structures *(Masters Adeline Surateau)*

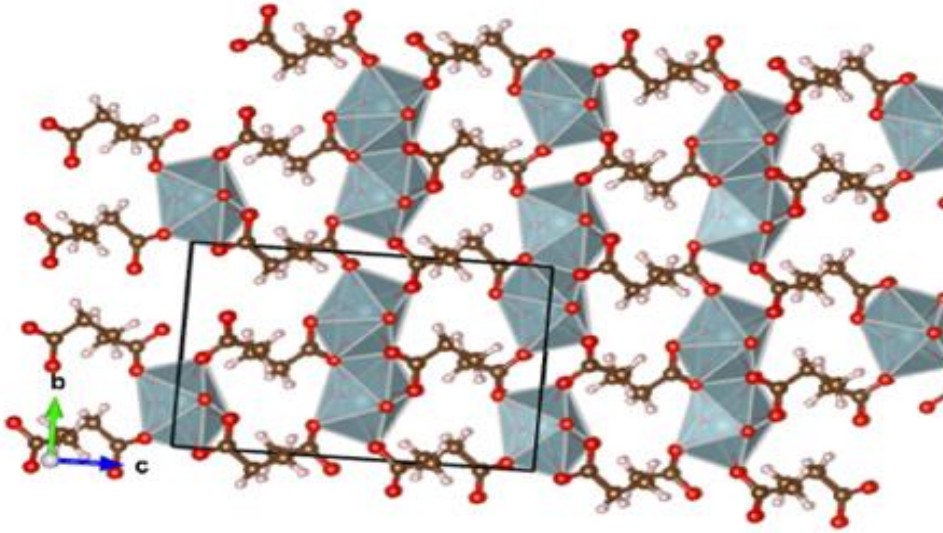
$[(NH_4)UO_2(glutarate)_{1.5}]_n$





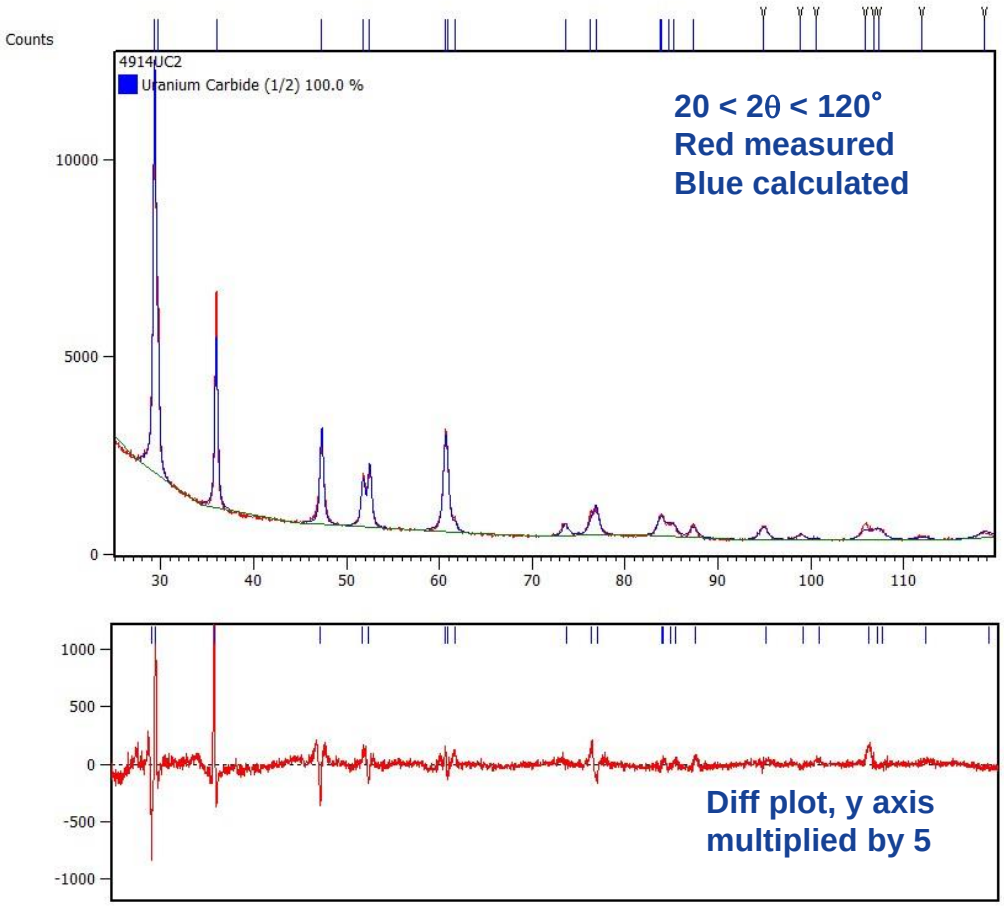
Δ, 240° C | - (NH_4)(glutarate)





Thermal treatment: precursors in SPS device

Powder diffractogram of UC_2



$20 < 2\theta < 120^\circ$
Red measured
Blue calculated

Diff plot, y axis multiplied by 5

Molecular precursor

$\Delta \downarrow$ 1400° C

$UO_2 + UC + UC_2 + C$

BUT for the therephthalate: only NC's of UC_2

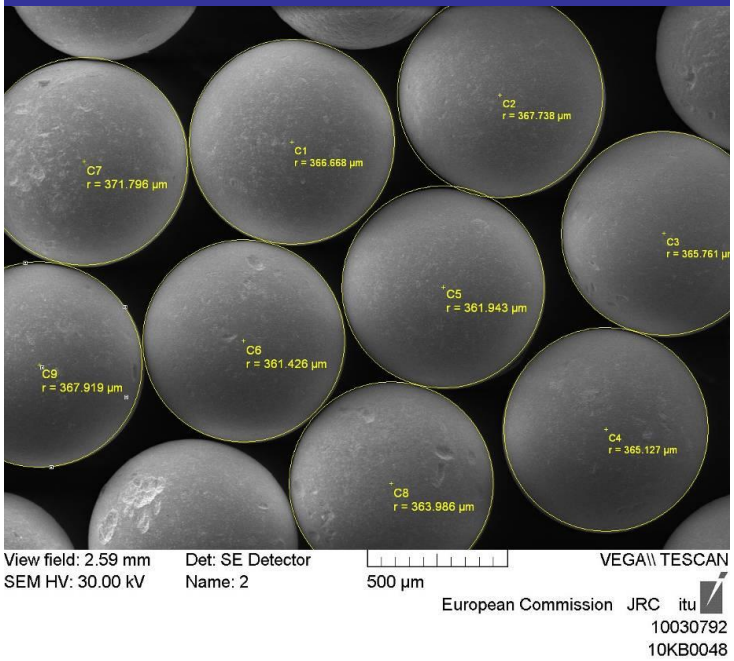
R (expected)/ %:	3.44
R (profile)/ %:	4.59
Space group (No.):	I 4/mmm
a/ Å:	3.52727(9)
c/ Å:	6.0078(3)

From FWHM of 6 peaks
Particle size: 16(2) nm

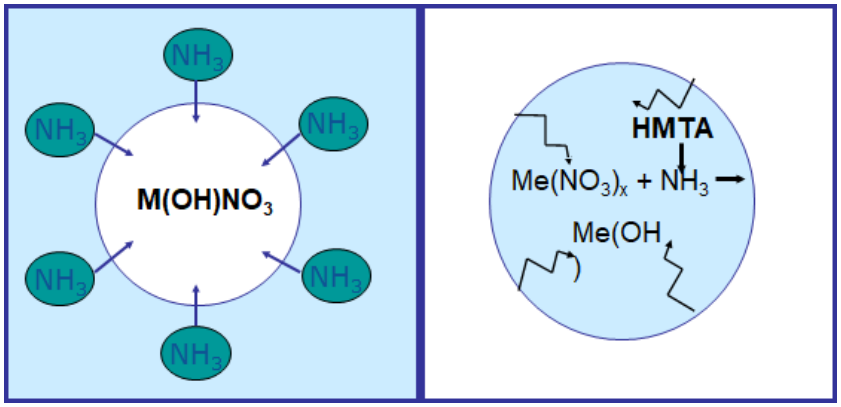
Possible to scale-up access to a pure nano crystalline UC_2 phase

Sol-gel based processes for fuel manufacturing

Vibro-sol (sphere-pac) process

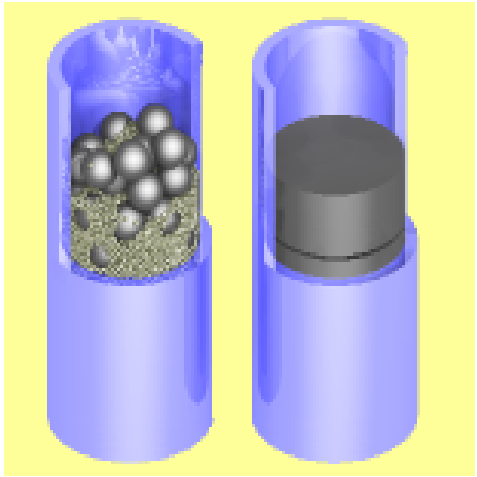


- ✓ Preparation of sol-gel derived microspheres (50-1000 µm)



internal gelation *external gelation*

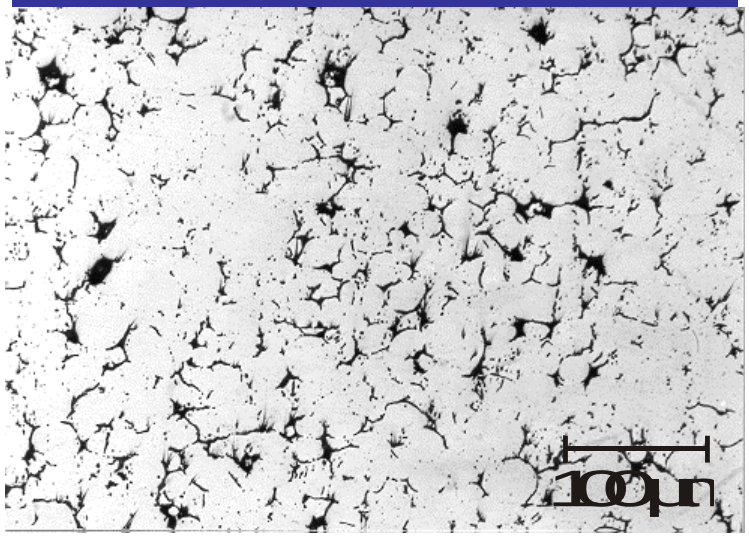
- ✓ The mixed oxide gel microphores are dried and sintered (TD≥96%)
- ✓ Subsequently packed in the cladding tube by vibratory compaction)



European Commission

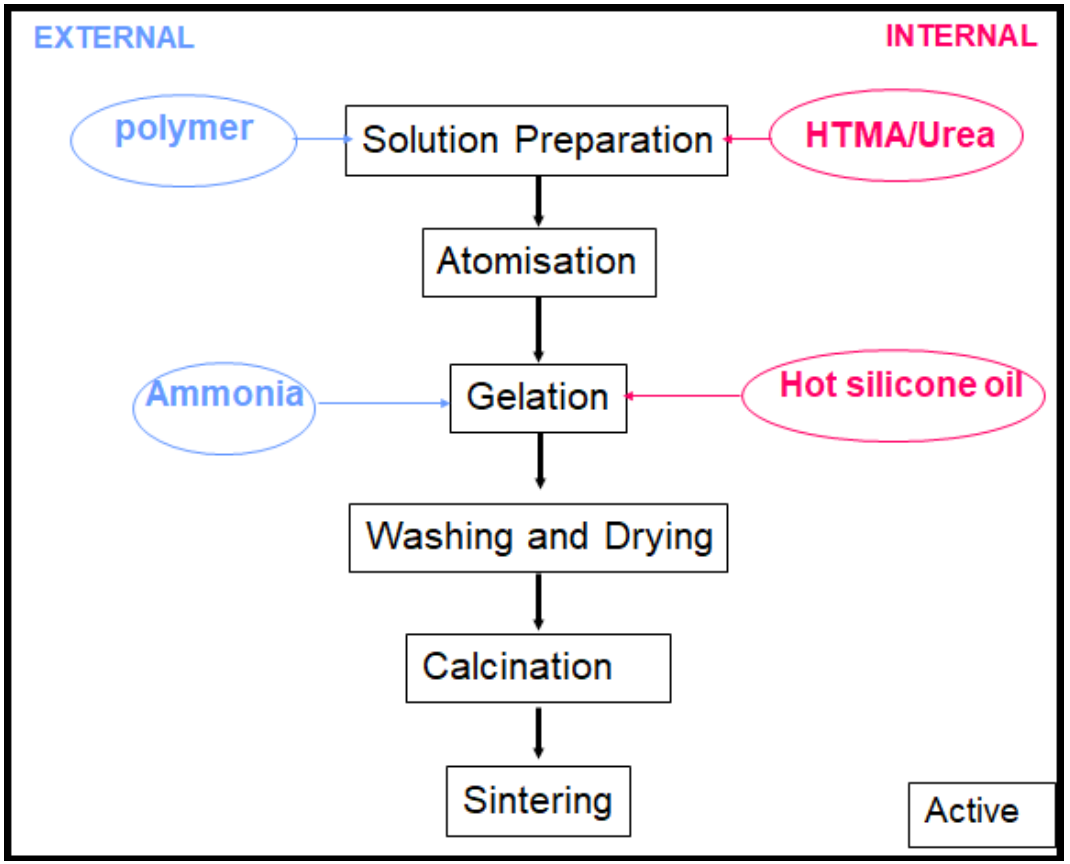
Sol-gel based processes for fuel manufacturing

Sol-gel microsphere pelletisation process



Sol-gel derived microspheres are directly compacted to pellets and sintered at ~1700 °C

- hard spheres → blackberry structure
- soft spheres → pellets w/o microsphere boundaries



Coated particle fuel

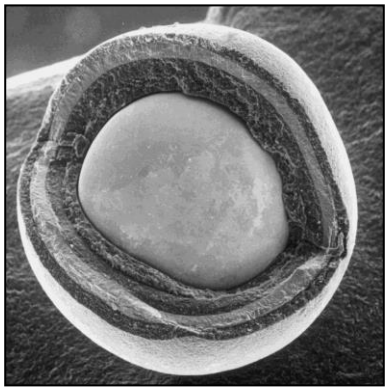
Fuel Kernel:
Provides fission energy (heat)
Retains a great part of fission products (FP)

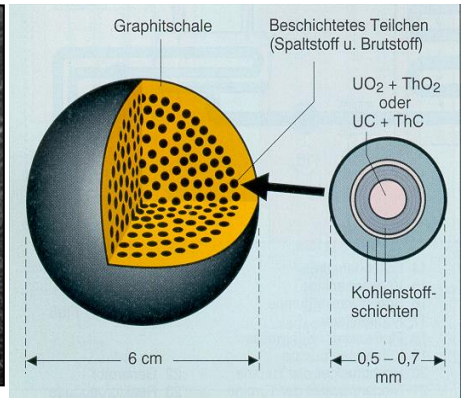
Buffer:
Protects main layers against FP recoil
Free volume for released fission gas (FG)
Accommodates Kernel swelling

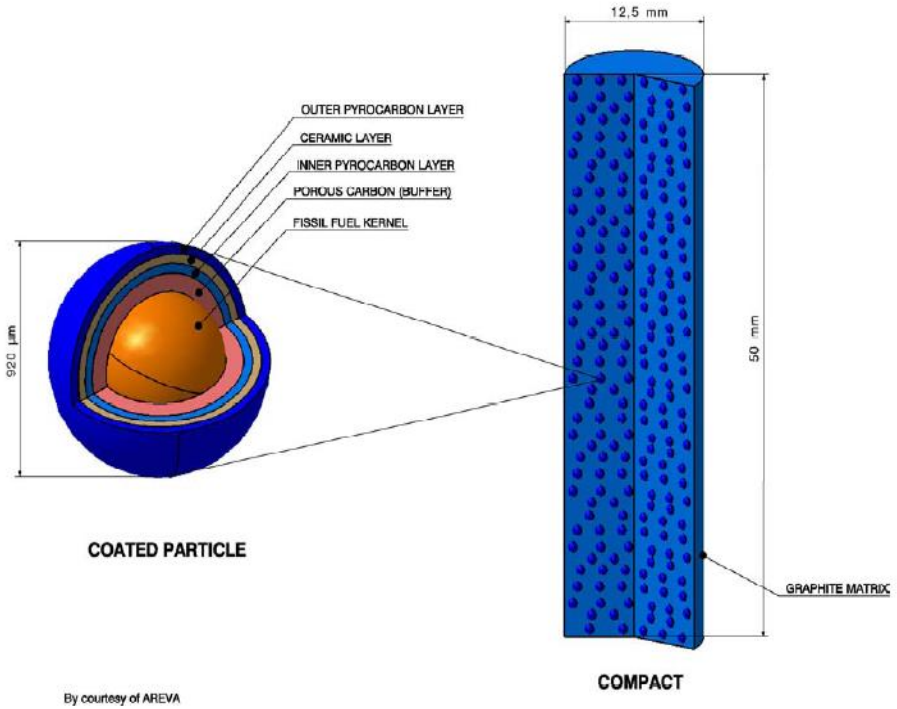
Inner PyC:
Prevents Kernel corrosion by chlorine during manufacture
Provides mechanical support for SiC
Retains FG

SiC:
Main load bearing member
Retains FG, volatile and metallic FP

Outer PyC:
Provides mechanical support for SiC
Provides FP barrier for particles with defective SiC
Provides bonding surface for compacting







Thank you for your attention!

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