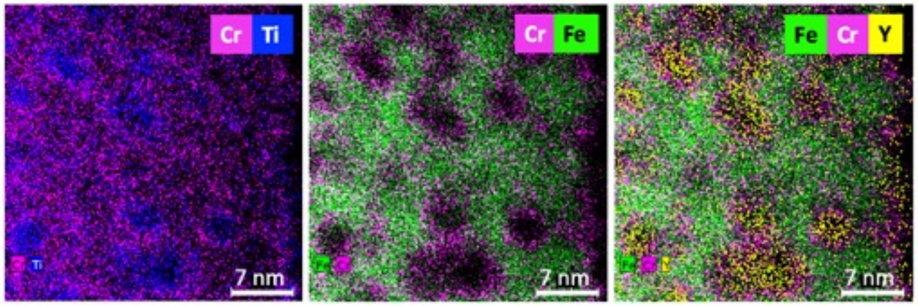
Polytech Paris-Saclay



The Nuclear Fuel – *From Ore to Waste*

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Outline

- Uranium physical and chemical data
- Uranium geology
  - Mining extraction
  - World resources
- Uranium fuels
- Uranium conversion
  - Transformation concentrate – hexafluoride
- Isotope enrichment
  - Mass spectrometry
  - Gas diffusion separation
  - Gas ultracentrifugation
  - Laser processes

Outline

Nuclear ceramics elaboration

- Role of the fuel
- Fuel subassembly
- Fabrication

Effects of in-reactor irradiation

- Modification of physical properties
- Chemical modifications: fuel composition after irradiation

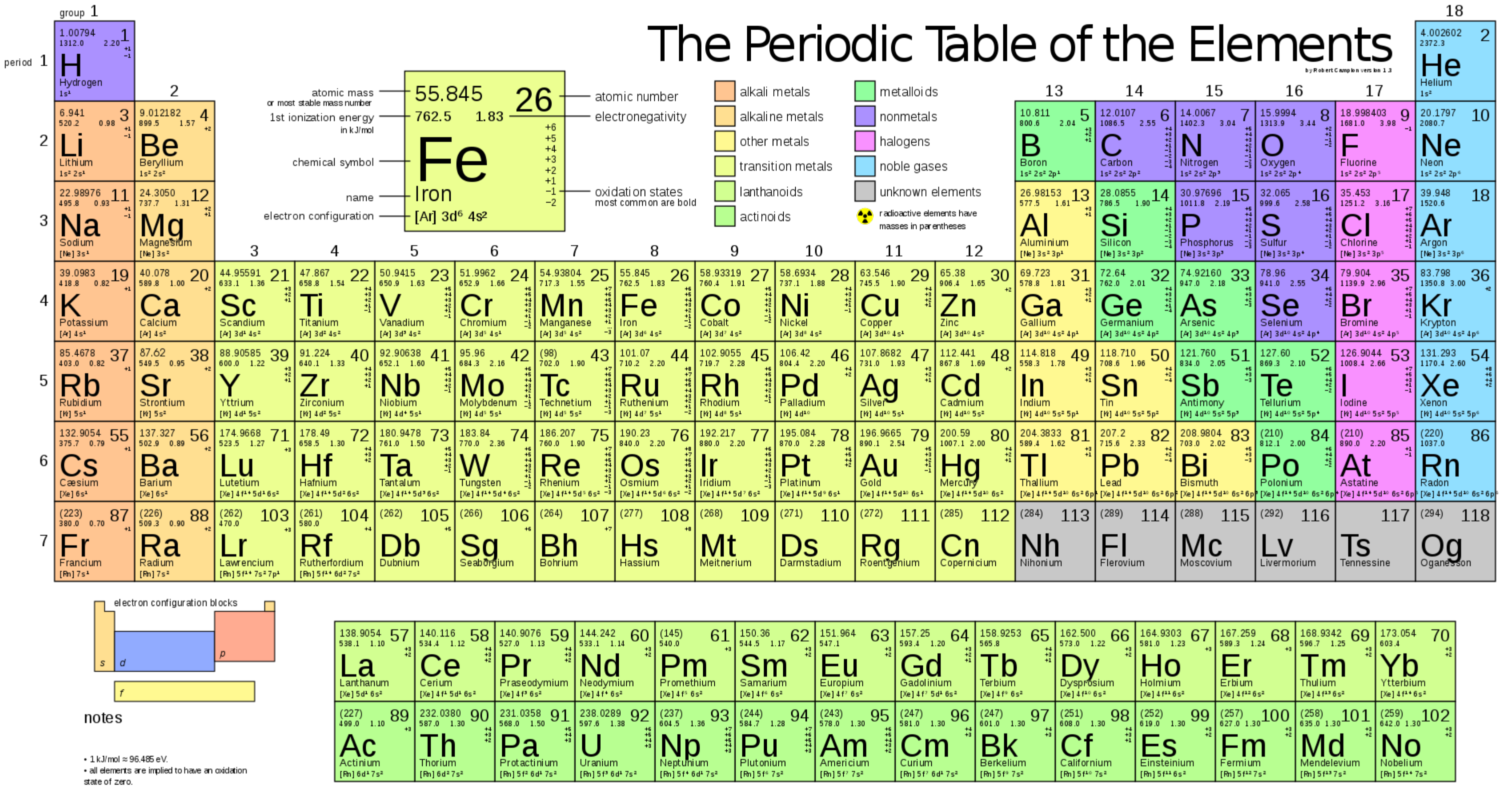
Reprocessing of nuclear fuels

- Methods
- U and Pu recycling possible strategies

Conditioning of reprocessed nuclear wastes

Uranium – Physical and chemical data

Actinides



The Periodic Table of the Elements

by Robert Campbell version 1.3

Key: atomic mass (or most stable mass number) 55.845; atomic number 26; 1st ionization energy in kJ/mol 762.5; electronegativity 1.83; chemical symbol Fe; name Iron; electron configuration [Ar] 3d⁶ 4s²; oxidation states +6 +5 +4 +3 +2 +1 −1 −2 (most common are bold)

- alkali metals
- alkaline metals
- other metals
- transition metals
- lanthanoids
- actinoids
- metalloids
- nonmetals
- halogens
- noble gases
- unknown elements
- ☢ radioactive elements have masses in parentheses

Z	Symbol	Name	Atomic mass
1	H	Hydrogen	1.00794
2	He	Helium	4.002602
3	Li	Lithium	6.941
4	Be	Beryllium	9.012182
5	B	Boron	10.811
6	C	Carbon	12.0107
7	N	Nitrogen	14.0067
8	O	Oxygen	15.9994
9	F	Fluorine	18.998403
10	Ne	Neon	20.1797
11	Na	Sodium	22.98976
12	Mg	Magnesium	24.3050
13	Al	Aluminium	26.98153
14	Si	Silicon	28.0855
15	P	Phosphorus	30.97696
16	S	Sulfur	32.065
17	Cl	Chlorine	35.453
18	Ar	Argon	39.948
19	K	Potassium	39.0983
20	Ca	Calcium	40.078
21	Sc	Scandium	44.95591
22	Ti	Titanium	47.867
23	V	Vanadium	50.9415
24	Cr	Chromium	51.9962
25	Mn	Manganese	54.93804
26	Fe	Iron	55.845
27	Co	Cobalt	58.93319
28	Ni	Nickel	58.6934
29	Cu	Copper	63.546
30	Zn	Zinc	65.38
31	Ga	Gallium	69.723
32	Ge	Germanium	72.64
33	As	Arsenic	74.92160
34	Se	Selenium	78.96
35	Br	Bromine	79.904
36	Kr	Krypton	83.798
37	Rb	Rubidium	85.4678
38	Sr	Strontium	87.62
39	Y	Yttrium	88.90585
40	Zr	Zirconium	91.224
41	Nb	Niobium	92.90638
42	Mo	Molybdenum	95.96
43	Tc	Technetium	(98)
44	Ru	Ruthenium	101.07
45	Rh	Rhodium	102.9055
46	Pd	Palladium	106.42
47	Ag	Silver	107.8682
48	Cd	Cadmium	112.441
49	In	Indium	114.818
50	Sn	Tin	118.710
51	Sb	Antimony	121.760
52	Te	Tellurium	127.60
53	I	Iodine	126.9044
54	Xe	Xenon	131.293
55	Cs	Cæsium	132.9054
56	Ba	Barium	137.327
57	La	Lanthanum	138.9054
58	Ce	Cerium	140.116
59	Pr	Praseodymium	140.9076
60	Nd	Neodymium	144.242
61	Pm	Promethium	(145)
62	Sm	Samarium	150.36
63	Eu	Europium	151.964
64	Gd	Gadolinium	157.25
65	Tb	Terbium	158.9253
66	Dy	Dysprosium	162.500
67	Ho	Holmium	164.9303
68	Er	Erbium	167.259
69	Tm	Thulium	168.9342
70	Yb	Ytterbium	173.054
71	Lu	Lutetium	174.9668
72	Hf	Hafnium	178.49
73	Ta	Tantalum	180.9478
74	W	Tungsten	183.84
75	Re	Rhenium	186.207
76	Os	Osmium	190.23
77	Ir	Iridium	192.217
78	Pt	Platinum	195.084
79	Au	Gold	196.9665
80	Hg	Mercury	200.59
81	Tl	Thallium	204.3833
82	Pb	Lead	207.2
83	Bi	Bismuth	208.9804
84	Po	Polonium	(210)
85	At	Astatine	(210)
86	Rn	Radon	(220)
87	Fr	Francium	(223)
88	Ra	Radium	(226)
89	Ac	Actinium	(227)
90	Th	Thorium	232.0380
91	Pa	Protactinium	231.0358
92	U	Uranium	238.0289
93	Np	Neptunium	(237)
94	Pu	Plutonium	(244)
95	Am	Americium	(243)
96	Cm	Curium	(247)
97	Bk	Berkelium	(247)
98	Cf	Californium	(251)
99	Es	Einsteinium	(252)
100	Fm	Fermium	(257)
101	Md	Mendelevium	(258)
102	No	Nobelium	(259)
103	Lr	Lawrencium	(262)
104	Rf	Rutherfordium	(261)
105	Db	Dubnium	(262)
106	Sg	Seaborgium	(266)
107	Bh	Bohrium	(264)
108	Hs	Hassium	(277)
109	Mt	Meitnerium	(268)
110	Ds	Darmstadium	(271)
111	Rg	Roentgenium	(272)
112	Cn	Copernicium	(285)
113	Nh	Nihonium	(284)
114	Fl	Flerovium	(289)
115	Mc	Moscovium	(288)
116	Lv	Livermorium	(292)
117	Ts	Tennessine	
118	Og	Oganesson	(294)

electron configuration blocks: s, d, p, f

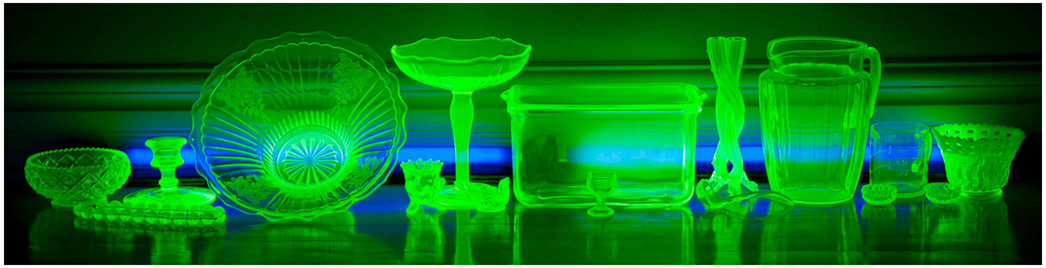
notes

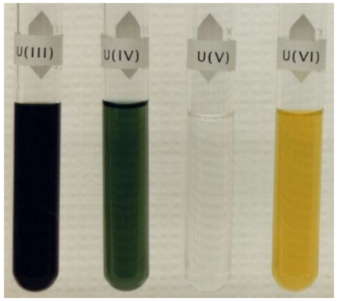
- 1 kJ/mol ≈ 96.485 eV.
- all elements are implied to have an oxidation state of zero.

Uranium – Physical and chemical data

Actinides - Uranium

- Electronic configuration of uranium [Rn] $5f^3\ 6d^1\ 7s^2$
- Oxidation states (III), **(IV)**, (V), **(VI)**
  - Reducing medium: (IV) (cation U^{4+}) [Rn] $5f^2$
  - Oxidising medium: (VI) (UO_2^{2+} uranyl ion) [Rn]
- Metallic state U
  - Melting point 1405.5 K; boiling point 4018 K
  - Structure: $T(\alpha \rightarrow \beta)$=941 K; $T(\beta \rightarrow \gamma)$=1047 K
    - α-U Orthorhombic structure (SG *Cmcm*); a = 284.79 pm; b = 585.80 pm; c = 494.55 pm
    - β-U tetragonal (SG $P4_2/mnm$); a=1076.0 pm; b=565.2 pm
    - γ-U cubic *bcc* (*Im*-3*m*); a=352.4 pm





Use of U glasses gets back to (at least) 79 AD (mosaic yellow glass 1% U in a Roman villa in the Bay of Naples, Italy)

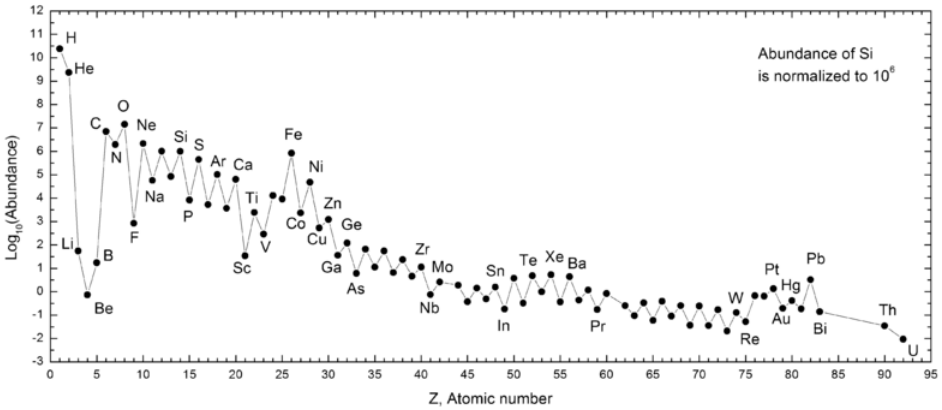
Uranium – Physical and chemical data

Physical data

- Three naturally-occurring isotopes: ^{238}U (99.28 %; half-life 4.5 × 10^9 y); ^{235}U (0.718 %; half-life 0.7 × 10^9 y); ^{234}U (0.0056 %; half-life 0.25 × 10^6 y)

Resources

- Little abundance : 2 to 3 ppm (2 to 3 g per ton of rock)
- Granites: 10-30 ppm
- Oceans: 3.3 mg par m^3



Uranium geology – Mining

Uranium-bearing minerals : more than 200 are known !

- Primary minerals: formation process in the deep underground – much of U quadrivalent
  - Uraninite, pechblende, uranothorianite: mixing of oxides with a composition in the range UO_2-UO_3 (mostly oxidised)
  - Silicates : coffinite $U(SiO_4)_{1-x}(OH)_{4x}$; uranothorite : $(Th,U)SiO_4$
- Secondary minerals: originating in the dissolution and re-precipitation of primary minerals – U hexavalent
  - Colourful crystals: yellow, orange, green
  - Carnotite : $K_2 (UO_2)_2(VO_4)_2$, 3 H_2O
  - Autunite : $Ca (UO_2)_2(PO_4)_2$, 10 to 12 H_2O
  - Tobernite : $Cu (UO_2)_2(PO_4)_2$, 12 H_2O

Uranium geology – Mining

Massive uraninite ‘eye’ surrounded with gummites

Tobernite crystals Cu $(UO_2)_2(PO_4)_2$, $12H_2O$

Autunite crystals Ca $(UO_2)_2(PO_4)_2$, $12H_2O$

Uranium geology – Mining

Value of the deposit depends on

- Quantity
- Geology, grade and mineralogy
- Mineralogy of associated metals and worthless materials
- Whether access is by underground or open-pit mining
- Number and costs of process stages required
- The cost of safely impounding residues

Uranium geology – Mining

Mining practice

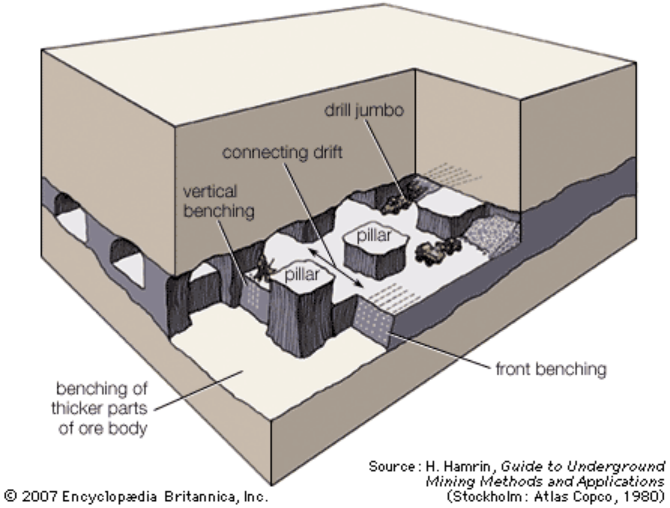
- Open-pit mining
  - Controlled blasting to break rocks into benches 5-20 m high, driven progressively into the face
  - Higher productivity, higher recovery, easier dewatering, safer working conditions, lower costs
  - Environmental impact greater both during and after the operating period

Open-pit mine in Niger (© ORANO group)

Uranium geology – Mining

Mining practice

- Underground mining
  - Advantageous below 200 m
  - Sedimentary ores are mined by the room and pillar method with stopes 2 m or more high
  - Vein-type ores are exploited by the cut and fill method (vein is cut into horizontal slices of 3-4 m high; when a slice has been mined it is back-filled with sand from the mill before the next slice is started)



Source: H. Hamrin, *Guide to Underground Mining Methods and Applications* (Stockholm: Atlas Copco, 1980)

Uranium geology – Mining

Radioactivity control

- Radioactivity is a guide during all stages from prospecting to ore concentration
- Location, extent and grade of a deposit are indicated by airborne, surface and drill-hole measurement (petrographic and chemical examination of drill cores also necessary)

Radiation risks

- External exposure mainly due to gamma-emitting nuclides in the U decay series
- Internal exposure: radon may migrate to rocks, be inhaled and deposit its daughter elements; radionuclides in dust that can settle into the lungs: workers must wear dust-filter masks and radiation-recording devices are used
- Robot-cutting in most richest mines

Uranium geology – Mining

Processing uranium ores

- Similar to other ores
- Choice depends on mineralogy of the ore and gangue, process of dissolution, desired product and the need for environmental precautions

Outline

- The ore is crushed and ground to a suitable size (in the range 0.1-0.5 mm)
- Leaching with sulphuric acid and an oxidant to convert U (IV) to the more soluble U (VI) (When the gangue material is basic leaching is made with a solution of Na_2CO_3 and $NaHCO_3$ to avoid excessive acid consumption)
- The solution is separated from the solid residue and purified by ion exchange or solvent extraction
- Final product precipitated from alkaline solution (NaOH, MgO, NH_4OH), dried or calcined: uranium ore concentrate (UOC or *yellowcake*) formation (U diuranate $Na_2U_2O_7$, MgU_2O_7, $(NH_4)_2U_2O_7$)

Uranium geology – Mining

Uranium ore concentrate (UOC) so-called ‘Yellow cake’ (© ORANO group)

Uranium geology – World resources

World reserves

- Reasonably Assured Resources (financially worthwhile less than 260 US$ per kgU): 4.72 × 10^6 tU (2019 data)
  - Countries : Australia 29%, Kazakhstan 12%, Russia 9%, Canada 8%, Niger 7%, Namibia 6%, South Africa 6%, Brazil 5%, United States 5%, China 4%
- Inferred resources (less than 260 US$ per kgU): 3.35 × 10^6 tU (2019 data)
- Identified resources = sum of both contributions, i.e. 8.07 × 10^6 tU (2019 data)

- Ultimate recoverable reserves: mean grade in the oceans 3.3 mg per m^3 - about 4.5 × 10^9 tU !

Uranium 2020: Resources, Production and Demand, OECD and NEA No. 7551; tU = tonne of heavy metal

Uranium geology – World resources

World production

- Demand is about 59.2 × 10^3 tU per year (2019) [considering 450 commercial nuclear reactors: power 396 GWe]; about 100 years of reserves guaranteed)
- Production : Kazakhstan 41%, Canada 16%, Australia 9%, Niger 7%, Namibia 6%, Russia 6%, Uzbekistan 4%, United States 3%, China 3%, Ukraine 2%
- World production in the period 1995-2005 is about 35 × 10^3 tonnes per year (US and Russian military stock reduction in the 90's)
- Expected demand in 2040 is about 60-100 × 10^3 tU depending on scenarios

Efficient use of resources (Th and U)

- Use of fertile materials ^{232}Th, ^{238}U that generate ^{233}U and ^{239}Pu by neutron capture
- R&D on Gen4 nuclear reactors crucial for the future of nuclear energy (fast breeder reactor)

Uranium 2020: Resources, Production and Demand, OECD and NEA No. 7551; tU = tonne of heavy metal

Uranium geology – World resources

French production

- No mine exploited today (maximum production rate was 2 × 10^3 tonnes per year in the 60's – closing down Jouac mine (Limousin region) in 2001)
- ORANO is nonetheless the second world producer (6 × 10^3 tonnes per year) – Its reserves amount to 225 × 10^3 tonnes per year (Niger, USA, Australia, central Asia, Canada) – more than 35 years of production)

Uranium fuels

Fuels

- Metal
- Uranium dioxide UO_2
- MOX: $(U,Pu)O_2$
- Special fuels: U_3Si; U_3Si_2; U_2Si_3
- Future fuels: UC, UN

Uranium ore concentrate

- Uranates
- Oxides: UO_2, U_3O_8, UO_3

Essential fabrication stages

- Purification of uranium
- ^{235}U-enrichment: conversion to UF_6
- Conversion to the required chemical form (e.g. metal, oxide)

Uranium fuels – Selected fuels

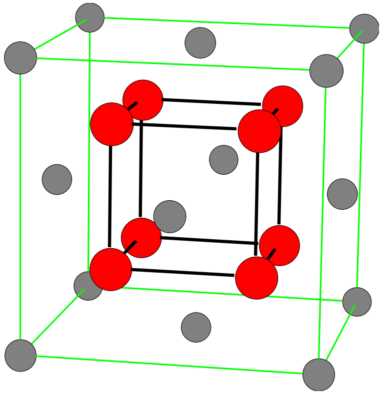
Fuel	U	UO_2	UC	UN
Density (g cm^{-3})	19.05	10.95	13.63	14.1
U density (g cm^{-3})	19.05	9.65	12.98	13.3
Melting T (K)	1406	3140	2623	3123
Thermal conductivity (W m^{-1} K^{-1})	27.6	7.4	25	20
Particularity	Phase transition at 941 K (expansion)	Stable under air and water when $T < 300$ K	Storage under inert gas – hydrolysis in hot water	Reactive with water – ^{14}C formation via $^{14}N(n,p)^{14}C$

Thermal conductivity: Cu 401 W m^{-1} K^{-1} ;Fe 80.2 W m^{-1} K^{-1} [300 K]

Uranium fuels – Uranium dioxide – Physical properties

Selected properties of Urania UO_2

- Crystallography: fluorite-type structure
- Cubic system space group *Fm*-3*m* – *fcc* lattice U atoms at (0,0,0); O at (1/4,1/4,1/4) and (3/4,1/4,1/4)
- Cell parameter *a* = 547.0 pm
- Specific mass 10.96 g cm^{-3}
- Very high melting point (3140 K)
- Low thermal conductivity: 7.4 W m^{-1} K^{-1} at 300 K (2.5 W m^{-1} K^{-1} liquid state)



Uranium fuels – Uranium dioxide – Physical properties

Selected properties of Urania UO_2

- Radiation-tolerant material
  - No phase transformation up to melting point
  - No evidence of amorphisation even under extreme irradiation conditions
- Relatively opened structure : possible incorporation of extra elements in cubic sites (inside an oxygen cube) and on U vacancies
  - Two fission fragments per one U atom
- (Very) Serious drawback: instability towards O_2 and H_2O while $T > 300$ K (U_4O_9, U_3O_7, U_3O_8 and U hydrates are the main oxidation products)

Uranium fuels – Uranium oxides - Fundamentals

Uranium oxides form two main groups

- Low O/U $\in$[2; 2.5]: *distorted fluorite-type* structure (e.g. UO_{2+x}, U_4O_{9-y}, U_3O_7)
- High O/U $\in$[2.5; 3]: *layered* structure with linear 'uranyl' groups (trans dioxo geometry) (e.g. U_3O_8, UO_3)

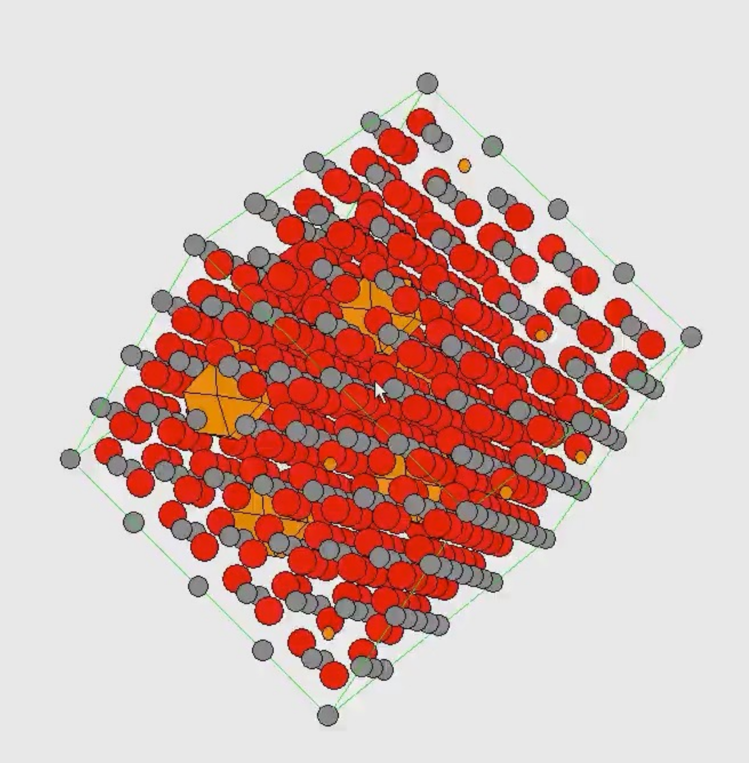
Distorted fluorite-type structure at low O/U

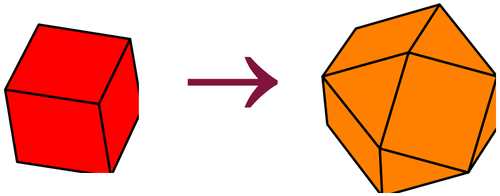
- Extra O atoms form anionic clusters embedded in the fluorite matrix
- Cluster are known to exist in UO_{2+x} and U_4O_{9-y} (Willis-type; anti-prism type cuboctahedral aggregates)

Uranium fuels – Uranium oxides – Description of U_4O_{9-y}

Crystal structure

- U_4O_{9-y} stands for $U_{64}O_{143}$ ($y \in [0.01;0.06]$)
- Almost no modification on the U sublattice
- Substitution of anionic cubes O_8 by anionic cuboctahedra O_{12}
- Ordered distribution of clusters in the SG *I*-43*d* coherently integrated within the fluorite matrix





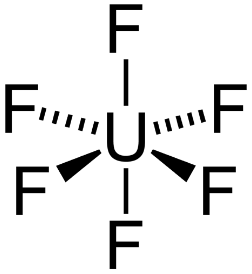
Isotope enrichment

Requirements

- PWR reactors: ^{235}U concentration around 3-5%

Methods

- Mass spectrometry: Lorentz force
- Difference in atomic mass between ^{235}U and ^{238}U
  - Gaseous diffusion though a membrane
  - Centrifuge enrichment
  - Both requires the conversion into the required chemical compound UF_6 (lowest melting point for halides; gaseous at 338 K; ^{19}F is the unique F isotope)



Isotope enrichment

Requirements

- PWR reactors: ^{235}U concentration around 3-5%

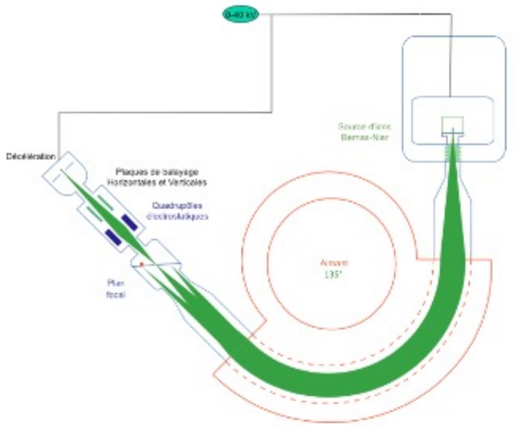
(Future) Methods

- Laser enrichment - Differences in electronic configurations (electromagnetic absorptions for ^{235}U and ^{238}U)
  - Atomic Vapour Laser Isotope Separation (AVLIS or SILVA *Séparation par Ionisation Sélective Atomique* in France)
  - Molecular Laser Isotope Separation (MLIS or SILMO *Séparation par Dissociation Sélective Moléculaire* in France)

Isotope enrichment – Mass spectrometry

Physical principle: magnet to separate isotopes using the Lorentz force

- First use as Calutron during the Manhattan project (*California University*-tron – University of Ernest Lawrence who supervised Los Alamos National Labs)
- Very high resolution magnet
- Isotopically-pure targets



SIDONIE separator (IJCLab, CNRS-Université Paris-Saclay)

Uranium conversion – From uranium ore concentrate to hexafluoride

Chemical conversion to UF_6: two distinct routes

- Dry process (purification at the end of the process – applies to oxides – first conversion of the uranate in oxide by calcination) [Applied Chemicals, USA]
  - U_3O_8 → reduction by NH_3 or H_2 → UO_2
  - UO_2 → hydrofluorination HF → UF_4
  - UF_4 → fluorination F_2 → UF_6
  - UF_6 purification by distillation

- Wet process (purification at the beginning of the process) [UK, France, USA, Canada]
  - Uranium ore concentrate → dissolution in HNO_3 → $UO_2(NO_3)_2$ impure
  - Impure nitrate → extraction with TBP → purified nitrate → de-nitration UO_3 → reduction by NH_3 or H_2 → UO_2
  - UO_2 → hydrofluorination HF → UF_4
  - UF_4 → fluorination F_2 → UF_6 pure
  - UF_6 crystallisation by condensation at 253 K (colourless crystal)

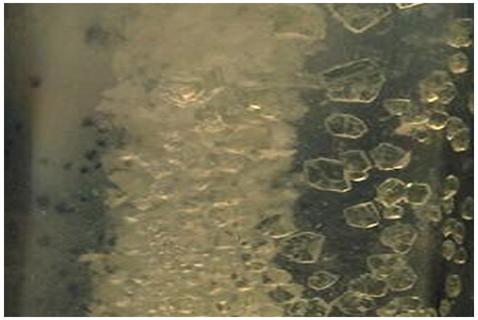
Uranium conversion – From uranium ore concentrate to hexafluoride

French plants : COMURHEX II since 2018 (ORANO group)

- Two factories: UF_4 elaboration (site de Malvési, Narbonne, Aude); UF_4 transformation to UF_6 (Pierrelatte, Tricastin, Drôme)
- Conversion capability: 15 × 10^3 tonnes per year (possible extension to 21 × 10^3 tonnes)

World conversion plants

- Angarsk (Russia): 20 × 10^3 tonnes per year
- Metropolis (IL, USA): 12.7 × 10^3 tonnes per year
- Port Hope (Ontario, Canada): 12.5 × 10^3 tonnes per year
- Springfields (UK) : 6.6 × 10^3 tonnes.$year^{-1}$



UF_6 crystals (© ORANO)

Isotope enrichment – Gaseous diffusion

Physical principle: $^{235}UF_6$ enrichment by difference in diffusion velocity through a membrane with small holes (10 nm)

- Thermal equilibrium at *T*: same average kinetic energy for all molecules ($E_C = 1/2\ mv^2$)
- Mean velocity of ^{235}U > mean velocity of ^{238}U
- Stage separation factor: Knudsen diffusion at low pressure

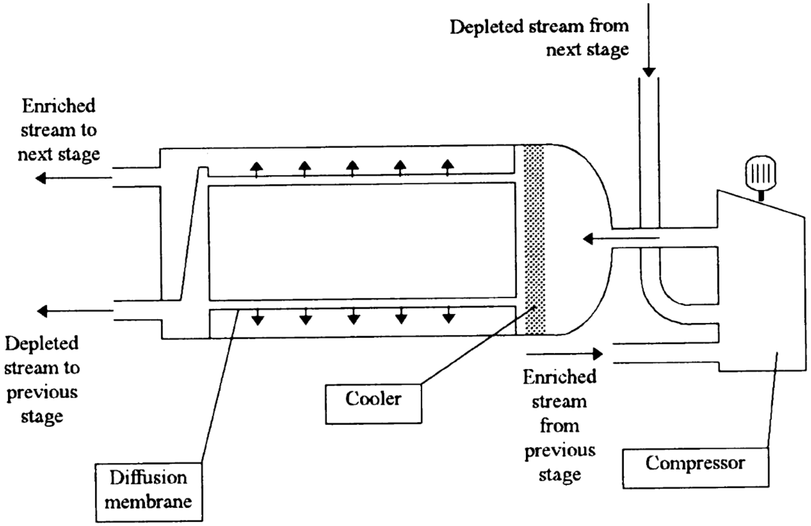
$$\alpha = \sqrt{\frac{M(^{238}UF_6)}{M(^{235}UF_6)}} = 1.0043$$

- Very low value of stage separation factor: series of collision barriers required (typically > 10^3)

Isotope enrichment – Gaseous diffusion

Essentials of a diffusion cascade stage

- Input flux
- Output 1 : enriched flux – to next stage
- Output 2 : depleted flux – to previous stage



Isotope enrichment – Gaseous diffusion

EURODIFF (European Gaseous Diffusion Uranium Enrichissement Consortium) factory – Georges Besse

- Consortium from five countries: France, Belgium, Spain, Iran, Italy
- The Pierrelatte (Tricastin) plant started in 1978; closure in 2012
- 1400 enrichment stages connected in series (stage separation factor at a given stage 1.002)
- Very high energy consumption due to gas compression: production required for 100 1-GW power plants needs a power of 3 GW (highest energy consumption plant in France)
- Large technical constraints: corrosion due to UF_6 – materials involve sintered alumina and steel protected by Ni
- Large capital investment necessitated

Isotope enrichment – Centrifuge enrichment

Georges Besse II – Physical principle: isotopic separation by means of the centrifugal force exploiting the small difference in mass between isotopes in vapour UF_6

- Gas injected in a spinning rotor
- Separation of isotopes: heavier move towards the periphery, lighter towards the centre
- Separation factor: $$\alpha = \exp\left\{\left[M({}^{238}UF_6) - M({}^{235}UF_6)\right]\frac{\omega^2 R^2}{2kT}\right\}$$
- Large separation factor ($\alpha \sim 1.2$) needed: speed rotation close to the resistance limit of used materials (C fibres speed > 800 $m.s^{-1}$)
- Plants: Russia (heavily enriched U production); consortium URENCO (Germany, The Nederlands, UK); Georges Besse II (since 2010)
- Main advantage: large reduction in energy consumption (5% of the gaseous diffusion)

Isotope enrichment – Laser enrichment

Physical principle : atomic absorption (specific of the electronic configuration of isotopes)

- Use of tuneable lasers
- Low operation cost

AVLIS (Atomic Vapour Laser Isotope Separation SILVA): selective ionisation of ^{235}U metal by tuning the laser light to very specific wavelengths; electrostatic or electromagnetic separation of ions

- Large separation factor >5
- Complex technology: several lasers to reach the ionisation energy (6 eV); U vapour is produced by electron bombardment; enriched and depleted fractions collected as condensed U
- Considerable research efforts (USA, France, Germany, Japan)

Isotope enrichment – Laser enrichment

MLIS (Molecular Laser Isotope Separation – SILMO): vibration frequency of the U-F bond depends on a given isotope

- $^{235}UF_6$ first excited by an infra-red laser
- Excited molecules are dissociated by an ultra-violet laser to give both $^{235}UF_5$ particles and fluorine gas
- UF_5 is a white powder easily separated by filtration from the depleted UF_6 gas
- Easier technology than the AVLIS process: main difficulty lays in the exact tuning of the laser wavelength
- Research efforts mainly in Japan

Nuclear fuel elaboration

Fuel design and properties have a strong impact on nuclear reactor performance and safety

- Low direct effect of the electricity price
- But major effect in case of breakdown leading to reactor shutdown
- Goal of the design and sizing of nuclear fuel elements is to guarantee their behaviour during regular and accidental conditions

Nuclear fuel elaboration

Main functions of the fuel

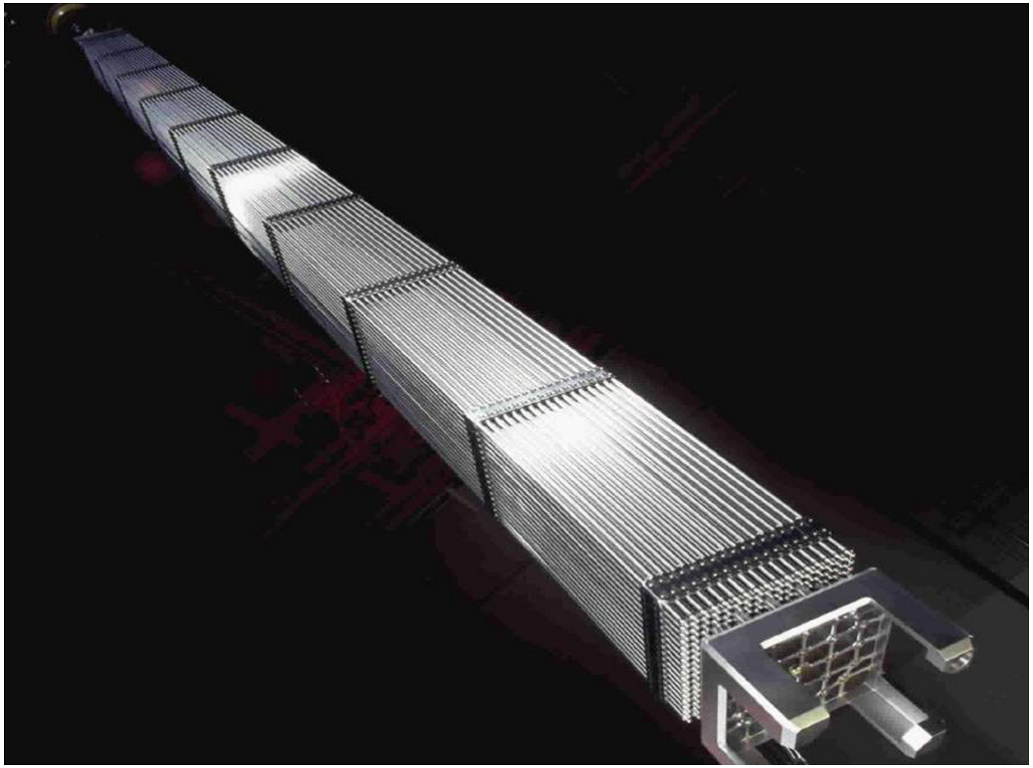
- Source of the heat by nuclear chain reaction
- First confinement barrier towards the radioactivity of the created fission products and actinide

PWR fuel subassembly

- Nuclear-grade ceramics form pellets
- Stack of UO_2 pellets is inserted into a zirconium alloy tube (Zircaloy-4: almost pure Zr with Nb, Fe, Cr, O; thickness 0.6 mm; external diameter 9.5 mm) – so called *fuel element*
- Stacks are assembled into a cage structure (pins are arranged in a 14 × 14 or 17 × 17 array)
- Control rod guide tube are fixed to top and bottom nozzles to monitor fissions (absorbers)
  - Metallic alloy AIC (80% Ag, 15% In, 5% Cd)
  - B_4C ceramic

Nuclear fuel elaboration

PWR fuel subassembly



Schematic of a PWR fuel element subassembly (© FRAMATOME group)

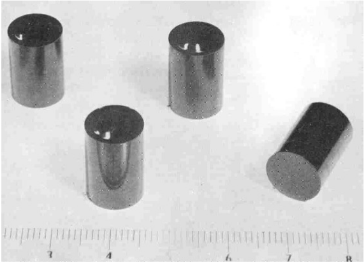
Nuclear fuel elaboration

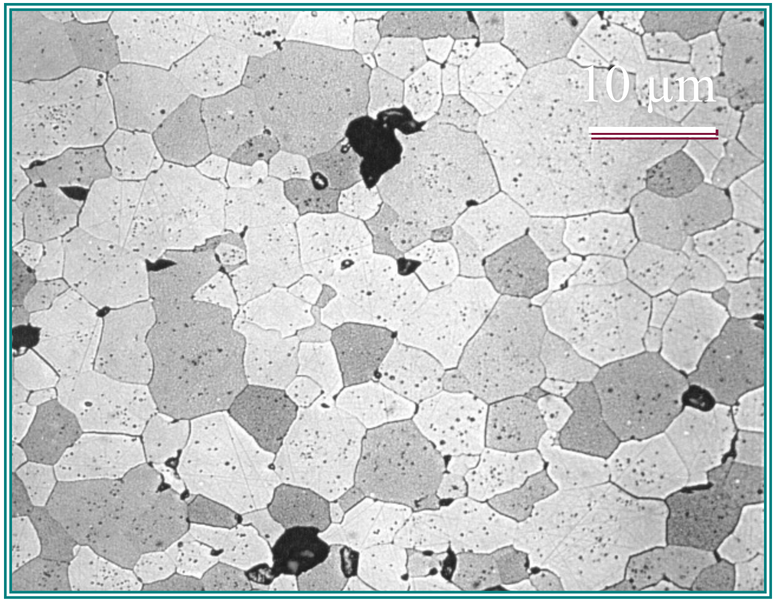
Main elaboration steps: dry conversion route to ceramic UO_2

- U (VI) reduction in U (IV) in a rotating furnace (with the vapour H_2O and H_2): $UF_6 + 2\ H_2O + H_2 \rightarrow UO_2 + 6\ HF$
- Mass density of UO_2 powder is adjusted by adding U_3O_8 and an organic compound to increase the porosity (typically 95% of its theoretical value)
- Uniaxial dry pressing to form UO_2 powder into the required pellet shape (8.2-mm diameter; 13.5-mm height)
- Sintering at 2000 K under a reducing atmosphere H_2
- Pellet finishing to fulfil design specifications (8.19-final diameter; gap between pellet and Zircaloy-4 cladding)
- Pellet inspection for quality (e.g. holes, cracks)

Nuclear fuel elaboration

Microstructure of the fuel





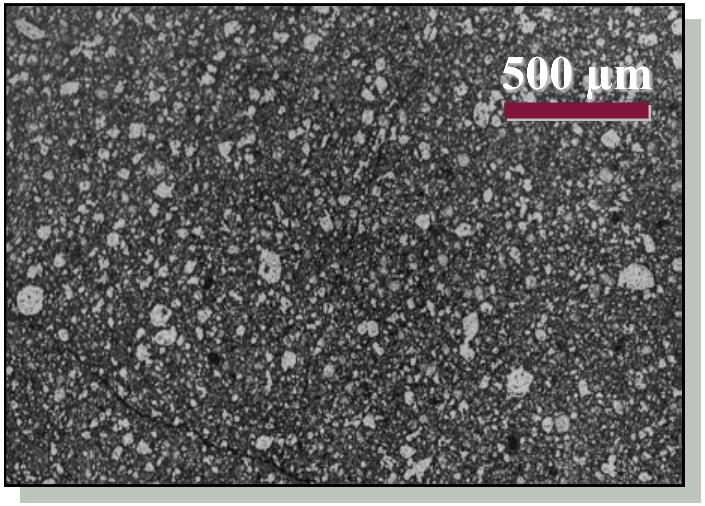
Micrograph of UO_2 after chemical attack revealing grains and boundaries

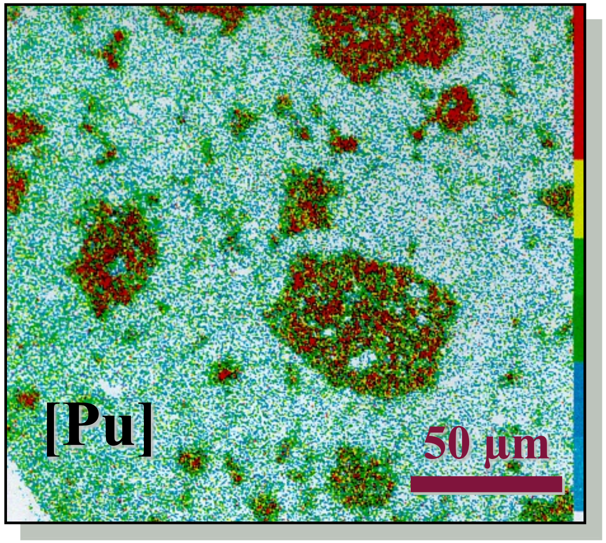
Nuclear fuel elaboration – Specific case of the MOX fuel

Mixing of UO_2 and $(U, Pu)O_2$ powders (typical size 50-100 µm) and sintering

Pu is an α emitter: fabrication in glove box

Typically 3 to 8 % PuO_2-rich aggregates distributed in the UO_2 matrix : large heterogeneity in the distribution of fissile nuclides

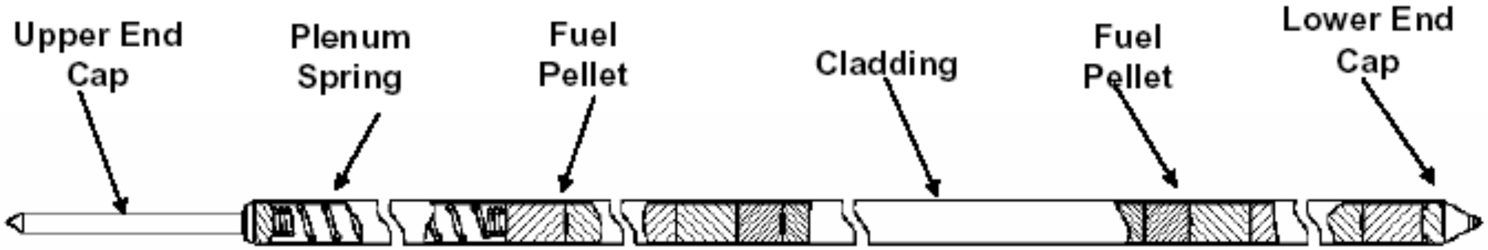




Nuclear fuel elaboration

Fuel element fabrication

- Sintered pellets incorporated into a Zircaloy-4 tube (External diameter 9.5 mm and around 4 m in height)
- A plenum spring (stainless steel) is inserted to maintain pellets during handling and transportation
- The tube is evacuated, flood with He gas to a specific pressure (25-30 bars) to improve thermal transfer, limit the creep of the Zircaloy-4 tube and avoid the oxidation of the fuel
- An upper expansion chamber to accommodate the release of fission gases
- End cap is welded
- Check for He leaks and pin inspection by X-radiography and gamma scanning



Schematics of PWR fuel element

Nuclear fuel elaboration

Fuel elaboration plants – technical constraints

- Radioprotection (UO_2 manipulation in glove box)
- Nuclear criticality safety to avoid a possible nuclear criticality accident

French plants

- *Franco-Belge de Fabrication de Combustible* (Romans-sur-Isère, Drôme – AREVA NP, FRAMATOME since 2018)
- Production capacity: 1000 tonnes of enriched UO_2 per year (1/3 of the world production)

Nuclear fuel elaboration

Assuming a typical 900-MW PWR power plant

- 265 pellets per single fuel element
- 264 fuel elements arranged in a 17 × 17 array
- 157 fuel element assemblies
- 11×10^6 pellets (i.e. 148 km and 81 tonnes)

Nuclear fuel elaboration

Gadolinium-doped fuel elements

- Some fuel elements are filled with Gd_2O_3-doped UO_2 pellets
- Gd (rare earth element) is a burnable poison (neutron predator: very large absorption cross section for odd nuclei)
- Strong decrease of the initial reactivity of the reactor after a partial or total fresh fuel refilling; progressive formation of even-Gd nuclei to compensate for the decrease of the fuel power
- Gd_2O_3-doped UO_2 pellets intentionally spread into the reactor to get a more homogeneous radial distribution of the power during a cycle (before fresh fuel incorporation)
- Typical amount of Gd is 8%: Gd is soluble into the UO_2 matrix

---

^{155}Gd (capture σ 61 kbarn), ^{157}Gd (254 kbarn): $^{157}\mathrm{Gd} + n \rightarrow {}^{158}\mathrm{Gd}$ (2 barn)

In-reactor irradiation effects

Nuclear fuels – UO_2, $(U,Pu)O_2$

Charged particles

- Fission fragments
  - Light fission fragment: kinetic energy 95 MeV; highly charged
  - Heavy fission fragment: kinetic energy 70 MeV; highly charged
- Alpha decay of actinide elements (uranium and transuranium elements – heavy actinides produced by neutron capture)
  - Alpha particle: kinetic energy is about 5 MeV
  - Heavy recoil nucleus (daughter nucleus) – typical kinetic energy is about 100 keV
- Electrons (and positrons) produced by fission product disintegration
  - Kinetic energy depends on nucleus but typically range from 10 keV to a few MeV

In-reactor irradiation effects

Nuclear fuels – UO_2, $(U,Pu)O_2$

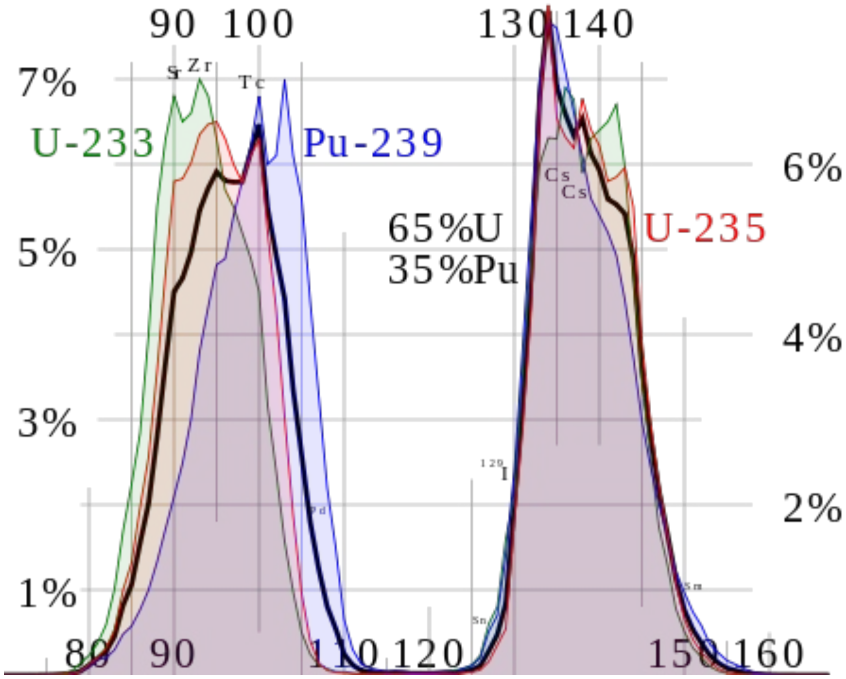
Neutral particles

- Neutrons produced by the fission reaction
  - Kinetic energy is about 2 MeV
- Gammas due to nuclei de-excitation
  - Energy is ranging from 10 keV to a few MeV
- Neutrinos and antineutrinos
  - Negligible interaction with matter

In-reactor irradiation effects

Evolution of the fuel during irradiation

- Neutron bombardment: ^{235}U and ^{239}Pu fission – 200-MeV energy per fission
- Production of two fission fragments
- One third of all elements are produced!



Fission yield versus mass number for ^{235}U, ^{239}Pu, ^{233}U

In-reactor irradiation effects

Main source of radiation damage: fission fragments

- Light fragment (95 MeV): projected range ~ 8 µm
- Heavy fragment (70 MeV): projected range ~ 6 µm
- Interactions processes
  - Electronic at the beginning of the trajectory: electronic excitations along the ion's path (cylinder of radius 10 nm)
  - Atomic (elastic) collisions at the end of the trajectory
- Target displacements (SRIM estimation)
  - Light fragment: ~ 5×10^4 displacements
  - Heavy fragment: ~ 7-8 $\times 10^4$ displacements

In-reactor irradiation effects – Useful physical quantities

Linear power

- Power generated per unit of fuel length
- In relation with the number of U atoms suffering fission per unit volume of fuel and per unit time

$$P_l = \frac{P}{L} = \left(\frac{N_{at}}{\Delta V \Delta t}\right) \Delta E_{1f} S$$

- Common unit: W cm^{-1}
- Typical value: P_l = 200 W cm^{-1}

In-reactor irradiation effects – Useful physical quantities

Burnup

- Total amount of energy extracted from nuclear fuel
- Expressed in terms of the heat energy produced per initial unit of fuel weight
- Common unit: GWd t^{-1} or MWd kg^{-1} (metric ton of initial heavy metal)
- Typical values: 50 GWd t^{-1} (burnup > 60 GWd t^{-1} already achieved)

In-reactor irradiation effects – Physical properties

Swelling of the fuel

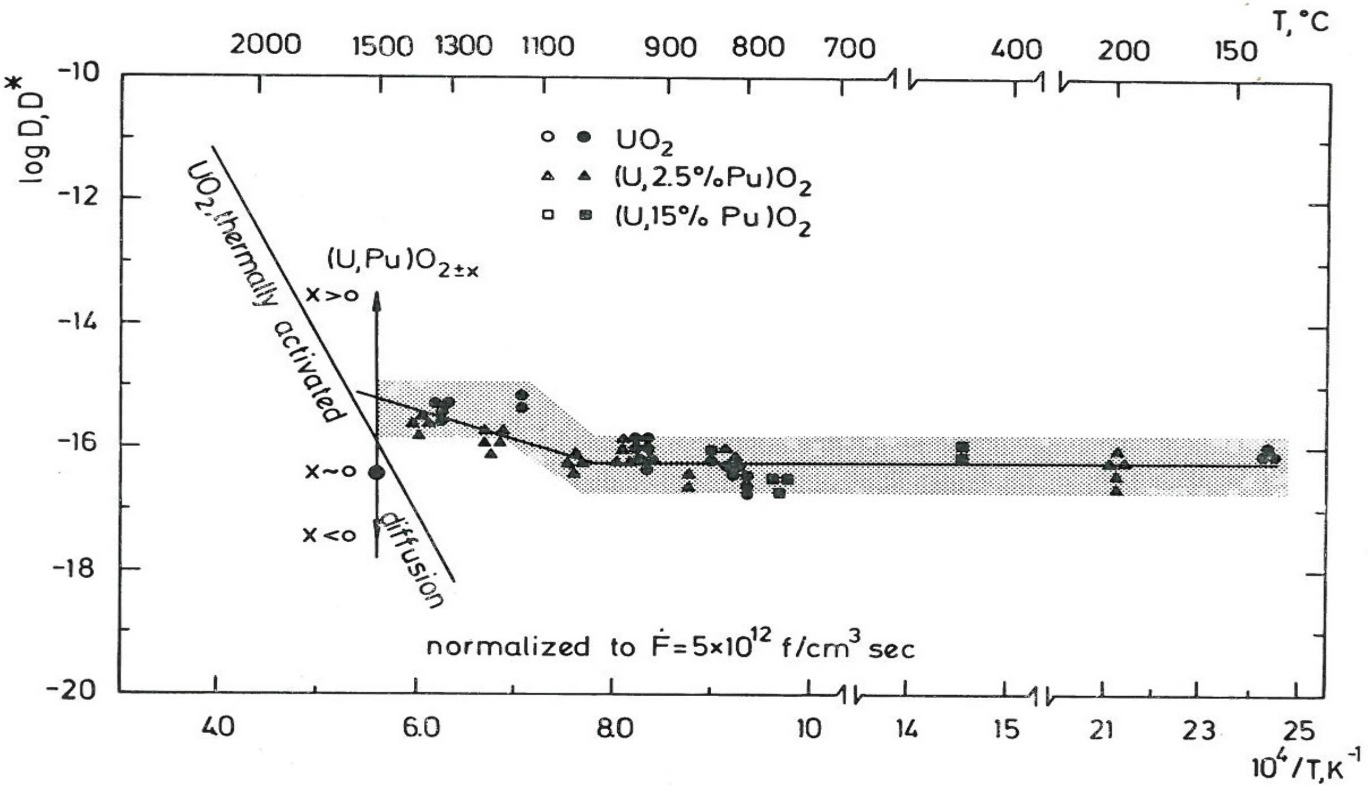
- Due to extra FP: 0.6-0.8% per 10 GWd t^{-1}
- Additional contribution from gas atoms at high *T* and high burn-up

Radiation-enhanced diffusion

- Out-of-irradiation: self-diffusion of U cations much lower than the self-diffusion of O anions ($D_O/D_U \sim 10^5$ at 1700 K): self-diffusion of U is rate-determining for high-*T* processes (e.g. creep, grain growth, sintering, densification)
- RED even at low *T* due to the slowing-down of fission fragments
- Diffusion of U during fission is temperature-independent below ~ 1273 K (radiation-enhanced metal diffusion) since U vacancies are produced by irradiation

In-reactor irradiation effects – Physical properties

Radiation-enhanced diffusion



Enhanced diffusion by ballistic collisions at low T (fission fragments and neutrons) due to the creation of U vacancies by irradiation

In-reactor irradiation effects – Physical properties

In-pile fuel densification

- From 94.5 to 95.5% of the theoretical density
- Interaction between fission fragments and small pores (disappearing of submicron pores) followed by annihilation of created vacancies on grain boundaries by radiation-enhanced diffusion

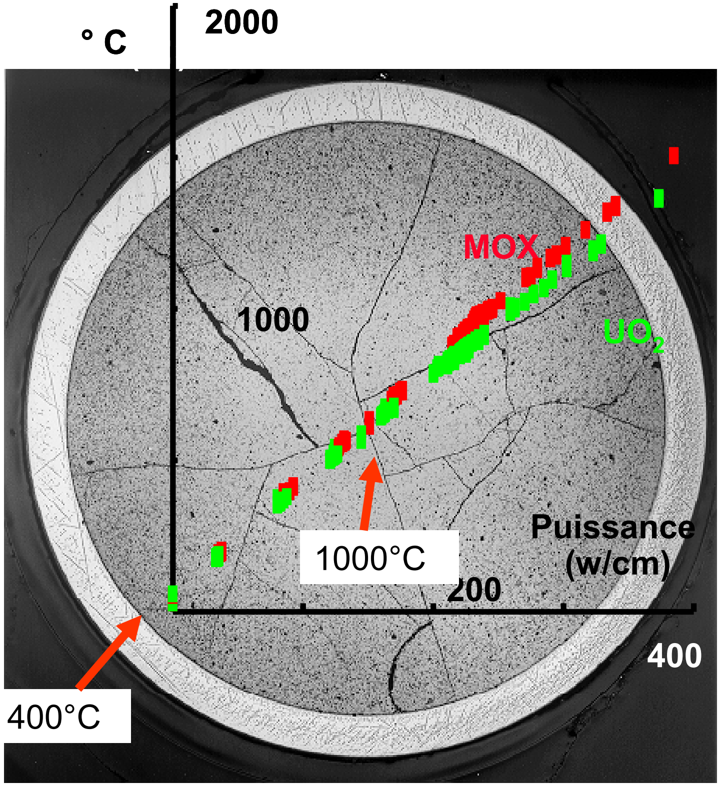
Radiation-enhanced creep

- Proportional to stress and to fission density
- Annihilation on grain boundaries of point defects created by fission (annihilation is stress-oriented)

In-reactor irradiation effects – Physical properties

Cracking due to a very large temperature gradient

- Normal conditions: *T* (surface) = 700 K; *T* (centre) = 1400 K (at P_l = 200 W cm^{-1})
- Accidental conditions: *T* = 2100 K (at P_l = 400 W cm^{-1})
- Thermal conductivity
  - Phonon contribution at low *T*
  - Electronic contribution starts around 1600 K



In-reactor irradiation effects – Physical properties

Thermal conductivity decreases with

- With increasing burn-up (main effect)
- Porosity enhancement
- Hyperstoichiometry x increase (composition of the fuel is UO_{2+x})
- Increasing the concentration of Pu and Gd

In-reactor irradiation effects – Physical properties

Thermal conductivity evolution

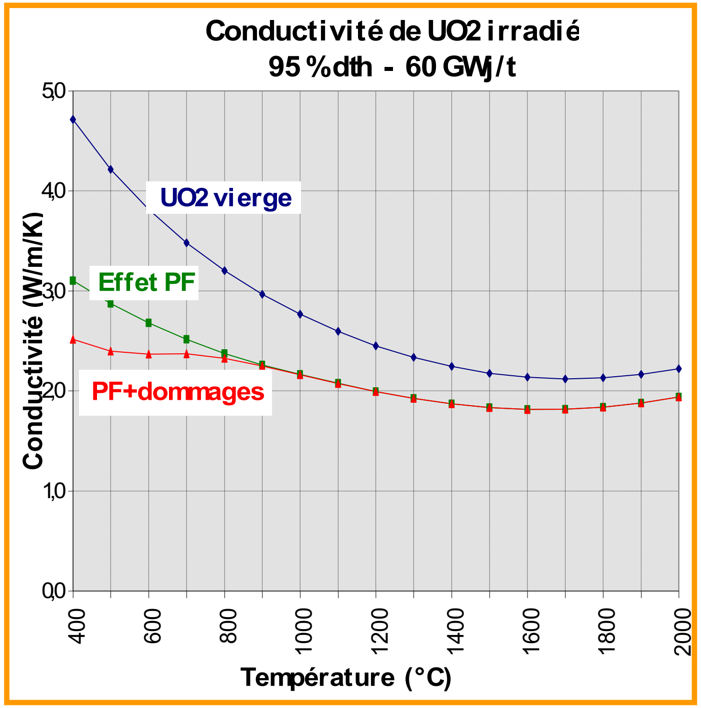
- Driven by phonons

In irradiated fuel: mainly due to the presence of fission products

- An hetero-atom acts as a diffusion centre for phonons
- At higher *T* the nucleation of FP precipitates decreases the number of scattering centres: enhancement of the conductivity

Due to radiation-induced point defects

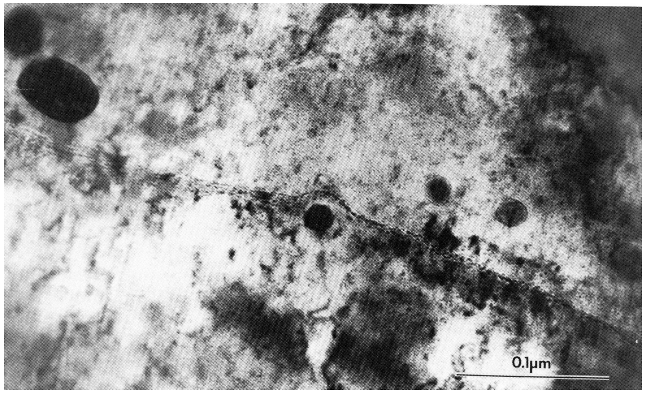
- Annealing stage for the cationic sublattice at 1000 K (U vacancy)

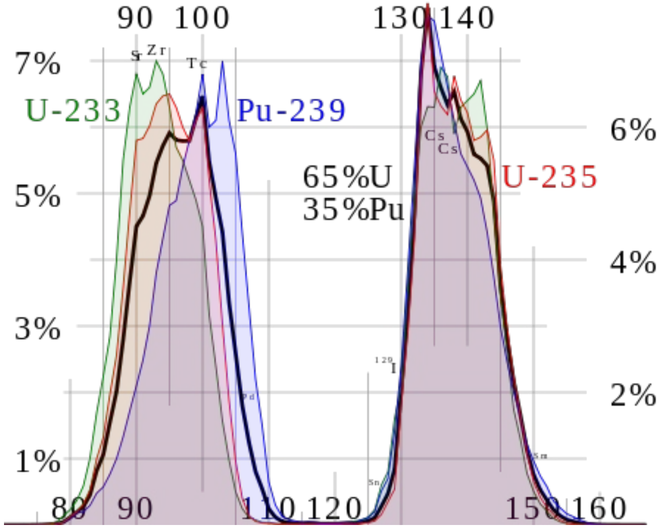


In-reactor irradiation effects – Fuel chemistry

Evolution of the fuel during irradiation

- Production of two fission fragments leads to the formation of two *fission products* (when they stop into matter)
  - β and γ emitters (Z ranges from 32 to 67 – two populations)
  - Relatively short half-life (< 30 years)
  - Radio-activity is dominated by decay of ^{137}Cs and ^{90}Sr (half-lives 30 and 29 years) after a few years





Fission gases and precipitates along a grain boundary in a spent fuel

In-reactor irradiation effects – Fuel chemistry

Evolution of the fuel during irradiation

- Neutron capture by heavy nuclei: transmutation – formation of trans-uranium elements (^{236}U, Pu, Am, Cm) : mainly α emitters (as well as n emitters for some of them)
  - Long half-life (dominating the fuel activity at long time)
- Some activation products due to fuel impurities

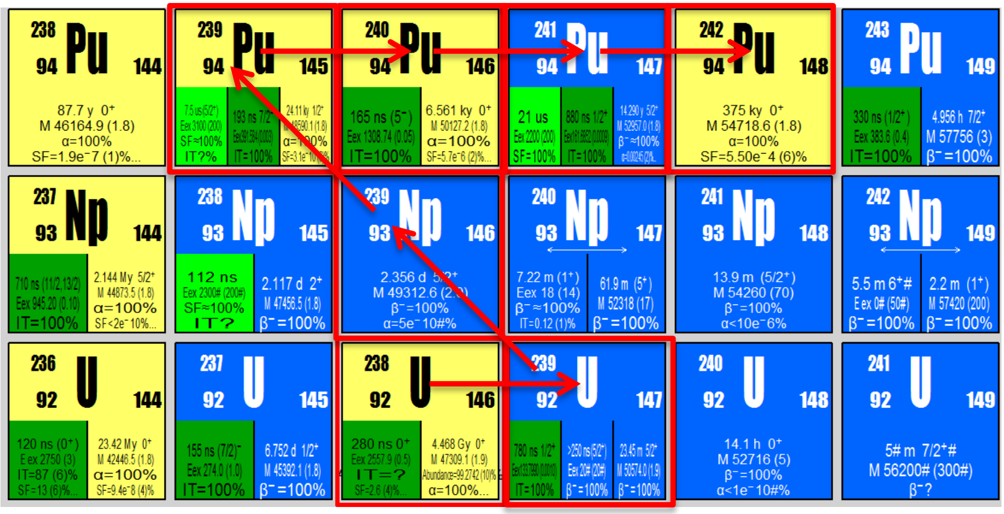
Dramatic modification of the fuel composition during irradiation

- Separation between the upstream and the downstream parts
- High residual heat (cooling is mandatory before any packaging or reprocessing)
- Very high radioactivity: 35×10^3 TBq t^{-1} (0.1 TBq t^{-1} before irradiation)
- Complex chemistry : large number of chemical elements
- System out of thermodynamic equilibrium

In-reactor irradiation effects – Fuel chemistry

Evolution of the fuel during irradiation

- Pu formation by neutron capture

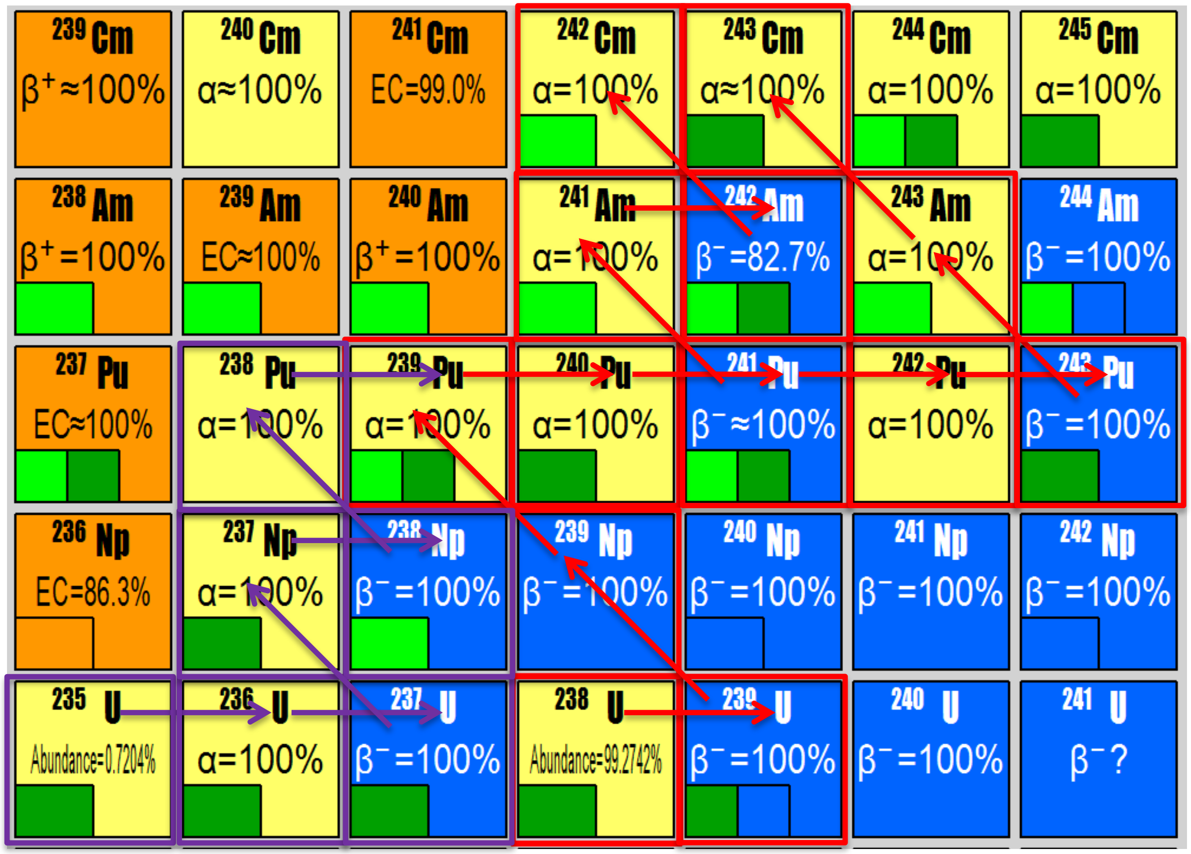


Neutron capture beta (-) beta (-) Neutron capture Neutron capture Neutron capture

In-reactor irradiation effects – Fuel chemistry

Evolution of the fuel during irradiation

- Am and Cm formation



^{239}Cm $\beta^+\approx100\%$	^{240}Cm $\alpha\approx100\%$	^{241}Cm EC=99.0%	^{242}Cm $\alpha=100\%$	^{243}Cm $\alpha\approx100\%$	^{244}Cm $\alpha=100\%$	^{245}Cm $\alpha=100\%$
^{238}Am $\beta^+=100\%$	^{239}Am EC≈100%	^{240}Am $\beta^+=100\%$	^{241}Am $\alpha=100\%$	^{242}Am $\beta^-=82.7\%$	^{243}Am $\alpha=100\%$	^{244}Am $\beta^-=100\%$
^{237}Pu EC≈100%	^{238}Pu $\alpha=100\%$	^{239}Pu $\alpha=100\%$	^{240}Pu $\alpha=100\%$	^{241}Pu $\beta^-\approx100\%$	^{242}Pu $\alpha=100\%$	^{243}Pu $\beta^-=100\%$
^{236}Np EC=86.3%	^{237}Np $\alpha=100\%$	^{238}Np $\beta^-=100\%$	^{239}Np $\beta^-=100\%$	^{240}Np $\beta^-=100\%$	^{241}Np $\beta^-=100\%$	^{242}Np $\beta^-=100\%$
^{235}U Abundance=0.7204%	^{236}U $\alpha=100\%$	^{237}U $\beta^-=100\%$	^{238}U Abundance=99.2742%	^{239}U $\beta^-=100\%$	^{240}U $\beta^-=100\%$	^{241}U $\beta^-?$

In-reactor irradiation effects – Fuel chemistry : Uranium inventory

Isotope	Unirradiated fuel	Spent fuel (47.5 GWd t^{-1})
238	959.6	925
235	40	7.4
234	0.4	0.2
236	0.0	5.4
U total	1000	938.0

In-reactor irradiation effects – Fuel chemistry : Plutonium inventory

Isotope	Spent fuel (47.5 GWd t^{-1})
238	0.4
239 *	6.1
240	2.8
241 *	1.5
242	0.9
Total Pu (* fissile part)	11.7 (7.6)

In-reactor irradiation effects – Fuel chemistry : Minor actinides

Chemical element	Spent fuel (47.5 GWd t^{-1})
^{237}Np	0.7
^{241}Am and ^{243}Am	0.5
^{244}Cm and ^{245}Cm	0.1
Total	1.3

In-reactor irradiation effects – Fuel chemistry : Fission products

Elements	Spent fuel (47.5 GWd t^{-1})
$67 \geq Z \geq 32$	48.7

^{235}U fissions: 67 %
^{238}U fissions (*via* ^{239}Pu and ^{241}Pu): 33%

In-reactor irradiation effects – Fuel chemistry : Fission products

	Elements	Amount (Kg t^{-1})	Fraction (%)
Gaseous PF	Kr Xe I	8.4	17
Alkali, alkaline earth metals	Rb Cs Sr Ba	7.7	16
Lanthanides	Y La Ce Pr Nd Pm Sm Eu Gd	14.5	30
Platinum group	Ru Rh Pd	5.9	12
Transition metals	Mo Zr Tc	11	22
Others	Se Br Ag Cd Sn Sb Te	1.2	3

In-reactor irradiation effects – Fuel chemistry

Fission product chemistry mainly imposed by the chemical potential of the fuel $\Delta G(O_2) = RT \ln(p(O_2))$

- Noble gases: Kr, Xe
- Metallic precipitates: Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te
- Oxides precipitates: Rb, Cs, Ba, Zr, Nb, Mo, Te
- In solution in UO_2: Sr, Zr, Nb, Y, & lanthanides: La, Ce, Pr, Nd, Pm, Sm

Fate of fission product strongly depend on the chemical state in the fuel (soluble versus soluble)

In-reactor irradiation effects – Behaviour of fission gases

Average mean number of gas atom generated per fission: 0.31 (including Xe and Kr)

- Xe is located in a Schottky trio (association of one U vacancy and two adjacent O vacancies – established by *ab initio* calculations)

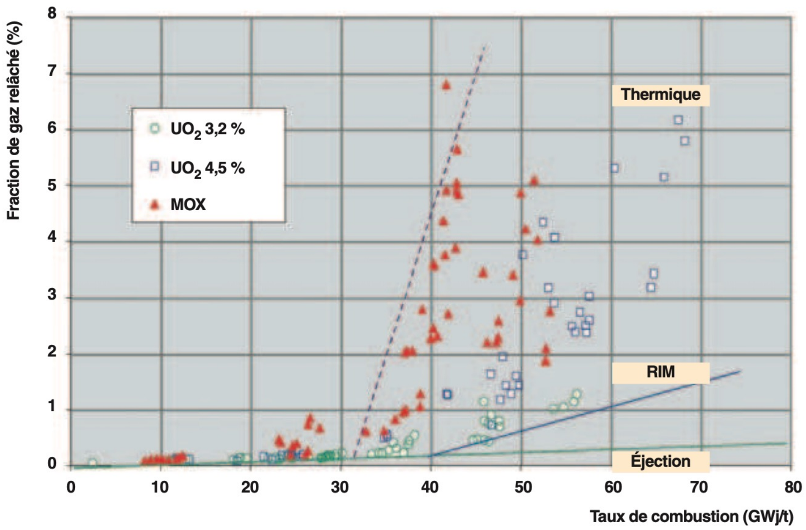
A large quantity of gas is incorporated in the spent fuel

- Too large internal pressure increase in case of total instant release (limitation of the burn-up increase)
- Actual release in PWR fuels is limited to a few percent (2-3 %)

In-reactor irradiation effects – Behaviour of fission gases

Athermal release mechanisms (*T* < 1300 K and release < 1 % - regular conditions)

- Recoil of fission fragments: some gas atoms are created near a free surface
- Ejection of previously created gas atoms located in the neighbourhood of a free surface due to the slowing-down of a fission product



Extra pressure in free volume may reach > 10 MPa at 60 GWd t^{-1}

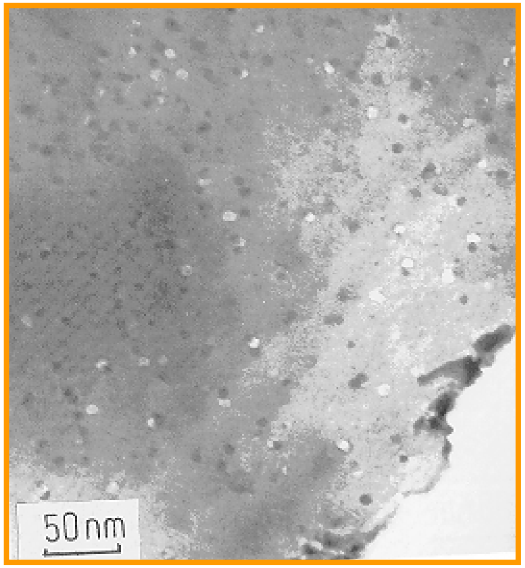
In-reactor irradiation effects – Behaviour of fission gases

Thermally-activated processes - TEM observations

- Formation of intragranular gas bubbles (1 to a few tens of nm; internal pressure ~ 1 GPa)
- Bubbles are generally associated with metallic precipitates
- Bubble re-solution by fission fragments: dynamical equilibrium

Thermally-activated processes - SEM observations

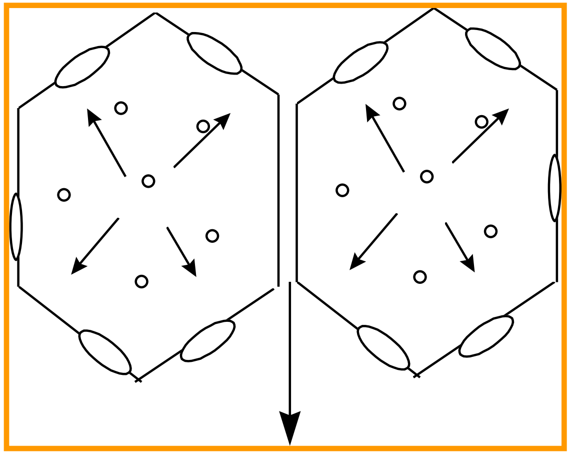
- Intergranular bubbles (typical size 1 µm) at large burn-up

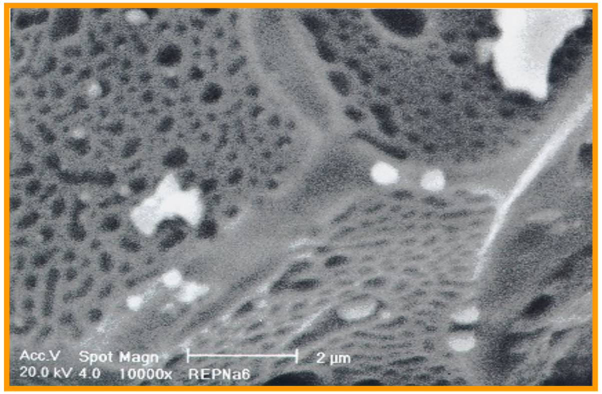


In-reactor irradiation effects – Behaviour of fission gases

Intergranular behaviour

- Intragranular gas bubbles diffuse towards grain boundaries
- Nucleation of intergranular bubbles (platelets) (generally associated with metallic precipitates)
- Growth of bubbles (and dissolution by fission fragment irradiation)
- Connexion of intergranular bubbles leading to a gas flow towards triple grain boundaries
- Formation of channels located at triple grain boundaries
- Gas release by percolation mechanism





SEM micrograph recorded on irradiated fuel: bubbles and channels at grain boundaries

In-reactor irradiation effects – High Burn-up Structure formation (HBS)

Large increase of the Pu formation near the fuel surface (rim zone)

- Neutrons with energy larger than thermal neutrons are absorbed at the rim by ^{238}U leading to the formation of ^{239}Pu)
- Neutron capture cross-section for ^{238}U exhibits resonances in the epithermal spectrum (up to 1 eV): the rim region is progressively enriched with fissile atoms
- Increase of the local burn-up in the rim zone (typically twice the mean burn-up and up to 150 GWd t^{-1} locally)

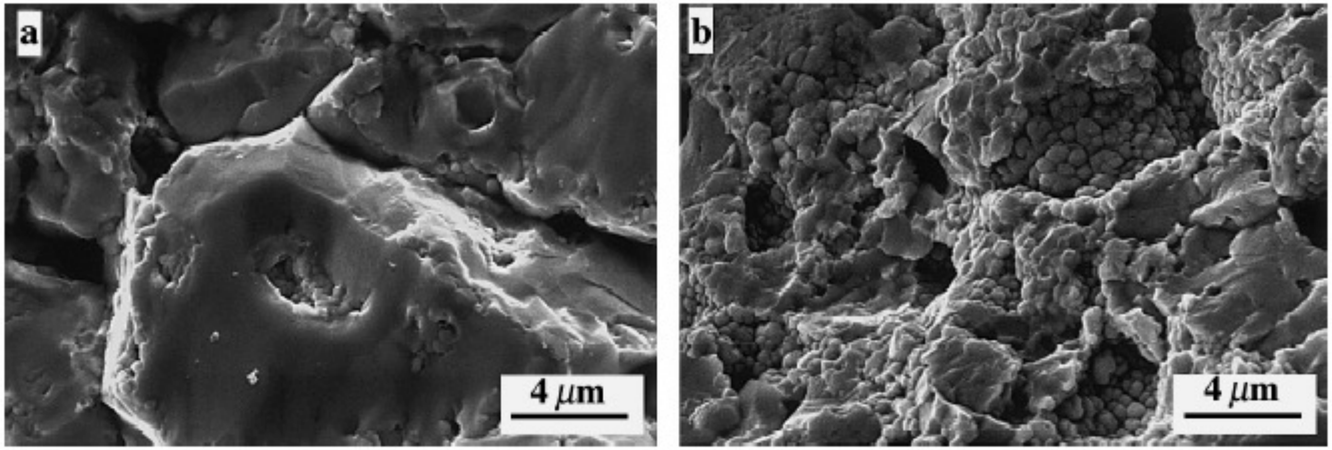
In-reactor irradiation effects – High Burn-up Structure formation (HBS)

Dramatic transformation of the fuel microstructure near the fuel surface (rim zone)

- Typical thickness ~ 200 μm from the fuel rim
- Formation of small grains (polygonisation phenomenon): initial size 10 μm; final size around 0.2 μm
- Low intragranular fission gas concentration
- Increased porosity (10-15 %)
- Presence of intergranular gas bubbles (typical size 1 μm)
- Increased gas release by diffusion along grain boundaries or breaking of grain boundaries

In-reactor irradiation effects – High Burn-up Structure formation (HBS)

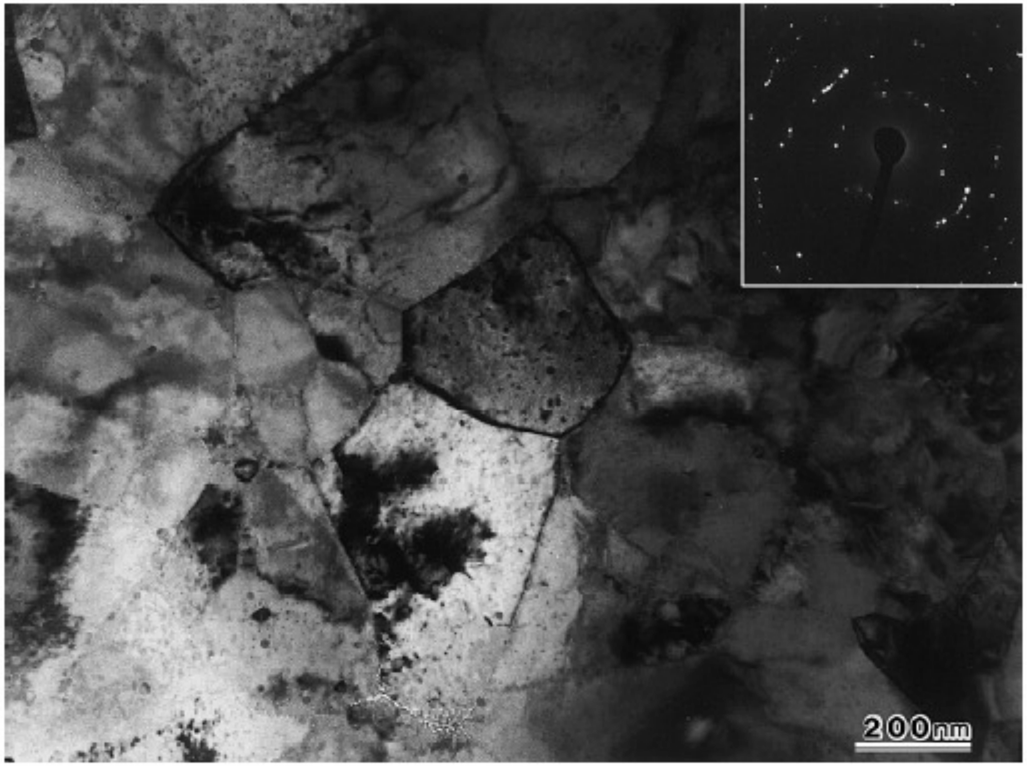
Dramatic transformation of the fuel microstructure near the fuel surface (rim zone)



SEM micrograph recorded on irradiated fuel in bulk (a) and rim (b) zones

In-reactor irradiation effects – High Burn-up Structure formation (HBS)

Dramatic transformation of the fuel microstructure near the fuel surface (rim zone)



TEM micrograph recorded on irradiated UO_2 in the rim zone

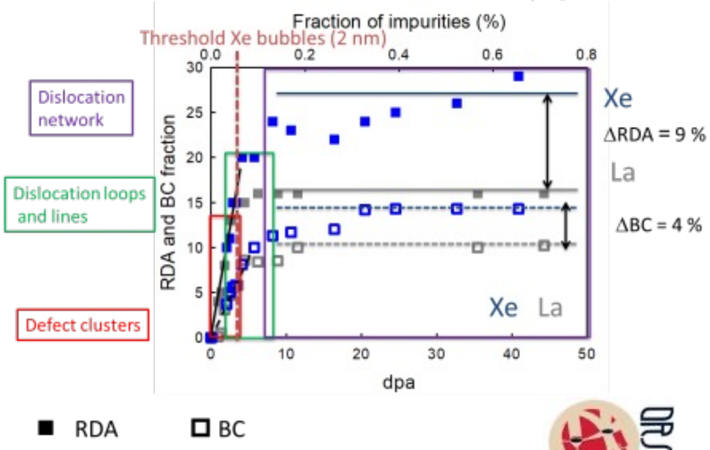
In-reactor irradiation effects – High Burn-up Structure formation (HBS)

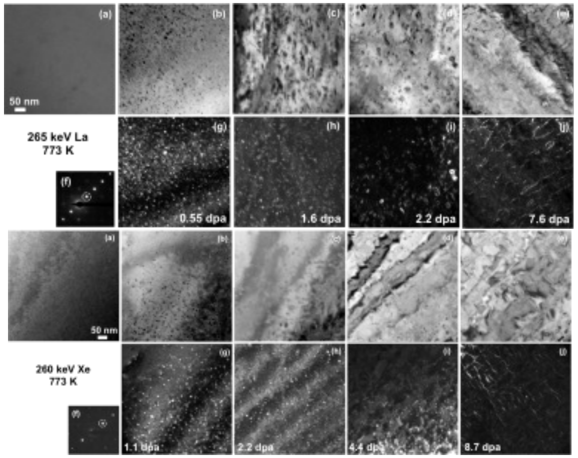
Experiments and modelling to understand this phenomenon – experimental and atomistic simulations (JANNuS-Orsay and GANIL)

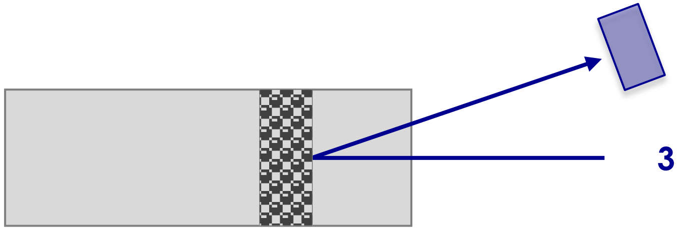
- Temperature relatively low at the rim
  - Recombination of radiation-induced defects not so effective
- Role played by the fission fragments: electronic and nuclear stoppings
  - Extreme electronic stopping induced a single crystal to polycrystal microstructural transformation
- Role played by fission products: chemical nature of incorporated elements
  - Comparison between soluble and insoluble elements

In-reactor irradiation effects – High Burn-up Structure formation (HBS)

- Formation mechanisms of the HBS at the fuel periphery (high porosity, small grain size; local increase of the Pu content)
- Parametric approach : burnup, T, chemistry of impurities, radiation defects and damage
- UO_2 single crystal as model system
- *In situ* irradiation/RBS-C or TEM at 773 K
    - First step is ballistic (radiation damage): same dpa for Xe and La, same evolution (clusters, dislocations, network)
      Second step : dramatic role of FP solubility – polygonization induced by nanometer-sized gas bubbles

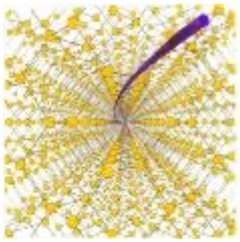






3 MeV He

Implanted UO_2 single crystal



Yara Haddad, PhD thesis (2017), Aurélie Gentils, Frederico Garrido

In-reactor irradiation effects

Remaining power after in-reactor irradiation (during the cooling period)

- Cooling in water-filled reactor store during ~ 1 year
- Wet cooling close to the reprocessing factory or interim storage location after transportation
- Water acts as both an effective shield and a good heat-transfer medium

Remaining power

- After 1 year : 0.05% of the nominal power
- 4 years (minimum time before reprocessing: 10^{-4} of the nominal power
- Main contributions: FP decay (80 % after 4 years); then α decay of actinides

In-reactor irradiation effects

Inventory after four years of cooling

- Fraction of U submitted to fission: 4.87%
- Fraction of U altered (^{236}U formation and minor actinide formation) : 1.08%
- Re-usable fraction : 94%
  - ^{238}U: 92.5%
  - ^{235}U: 0.74 %
  - Fissile Pu: 0.76%

In-reactor irradiation effects

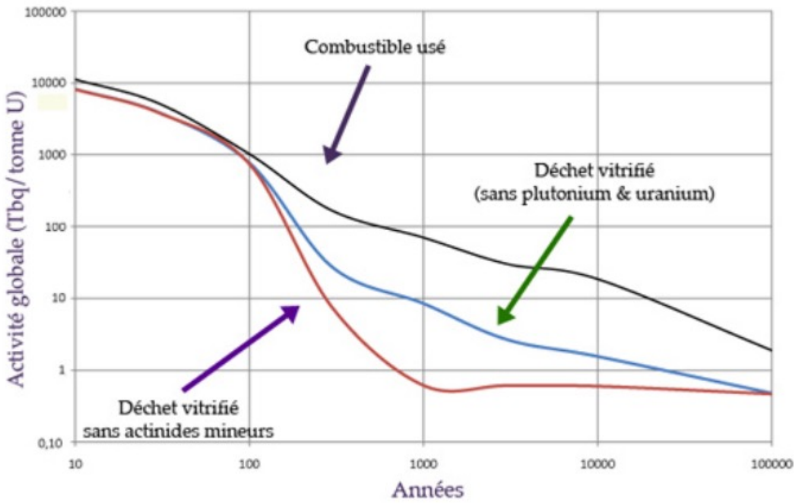
Uranium recycling

- 94% may be *a priori* recycled in PWR reactors
- Today's solution: extraction of FP and minor actinides by reprocessing (^{236}U, ^{238}Pu, ^{240}Pu, ^{242}Pu remain unseparated and are not fissile in PWR reactors)
- Future trends
  - Enhanced actinide separation processes for U and Pu isotopes
  - Transmutation of heavy actinides in fast neutron reactors: GEN4 nuclear power plants

Reprocessing of nuclear fuels

Main goals

- Recover residual uranium and plutonium for re-use
- Conditioning the nuclear wastes (fission products and minor actinides) into suitable forms for long-term interim or final disposal
- Reducing the radioactivity of nuclear wastes



Natural activity of uranium : 0.025 TBq t^{-1}

Reprocessing of nuclear fuels

Reprocessing principles

- Dissolution of spent fuel in concentrated nitric acid HNO_3
- Selective extraction (liquid-liquid extraction) of metallic cations U and Pu by an organic extracting solvent TBP (tributylphosphate)

$$M_{aq}^{n+} + nNO_{3\,aq}^{-} + 2\,TBP_{org} \leftrightarrow [M(NO_3)_n, 2TBP]_{org}$$

$$UO_{2\,aq}^{2+} + 2\,NO_{3\,aq}^{-} + 2\,TBP_{org} \leftrightarrow [UO_2(NO_3)_2, 2TBP]_{org}$$

$$Pu_{aq}^{4+} + 4\,NO_{3\,aq}^{-} + 2\,TBP_{org} \leftrightarrow [Pu(NO_3)_4, 2TBP]_{org}$$

- Solvent capability to extract a metallic cation M defined as its partition coefficient $D_M = [M]_{org}/[M]_{aq}$ (D_M increases while increasing $[NO_3^-]$)
- Valence (III) and (V) metallic cations barely extractible since $D_M \sim 10^{-3} – 10^{-2}$
- Valence (IV) and (VI) metallic cations are easily extracted since $D_M \sim 10 – 30$

Reprocessing of nuclear fuels

Behaviour of fission products

- Gaseous FP are evacuated during the dissolution
- Alkali & alkaline earth metals: non extractible
- Lanthanides: exhibit (III) valence state and cannot be extracted
- Platinum group metals: Rh and Pd can barely be extracted; Ru has a very complex chemistry from (II) to (VIII) valence states
- Transition metals: only Tc (VI) can be extracted and causes problem

Reprocessing of nuclear fuels – Main steps

Cutting of fuel subassemblies

- Performed in hot cells
- Opening of the fuel zirconium claddings

Nitric acid dissolution – liquor formation

- Use of boiling HNO_3 3 $mol.L^{-1}$
- Uranium forms soluble U (VI)
- Plutonium forms soluble Pu (IV)
- FP oxides (Alkali & alkaline earth metals, lanthanides) and (III) valence state minor actinides (Am, Cm) are easily solubilised
- Other PF are either insoluble or partially soluble (Mo, Zr); Tc and I have a complex behaviour

Nitric acid dissolution – Overview

- Almost all atoms of U, Pu and minor actinides are solubilised
- 80 % of FP (remaining 20%: gases, platinum group metals, Zr, Tc, Mo)

Reprocessing of nuclear fuels – Main steps

Clarification of the dissolution solution

- Cutting debris (chip)
- Platinum group metal particles and partial dissolution of Tc, Mo and Zr
- Liquor centrifugation
- Small particles are separated and mixed with fission products to be vitrified

Treatment of dissolution gases

- Separation and condensation of nitric vapours into HNO_3
- Atmospheric release of gaseous fission gases
- Specific treatment regarding ^{129}I: soft beta emitter ($T_{1/2}=16 \times 10^6$ y) – trapped and released into the see

Reprocessing of nuclear fuels – Main steps

Extraction operations – PUREX process (*Plutonium Uranium Refining by Extraction*)

- Process developed during 50's in USA and modified in Europe for military Pu at first
- Extraction cycle
  - Extraction of a given element into the organic phase (TBP)
  - De-extraction of the extracted element into the aqueous phase
  - Solvent re-generation
- Input liquor: U (200 $g.L^{-1}$), Pu (2 $g.L^{-1}$), minor actinides (100%), FP (80%); valence states: U (VI), Pu (IV), Np (V), Am (III), Cm (III); activity: 7.4 $TBq.L^{-1}$

Reprocessing of nuclear fuels – Main steps

Extraction operations – PUREX process (*Plutonium Uranium Refining by Extraction*)

- First cycle: co-extraction of U and Pu from others FP – high acidity (3 mol.L^{-1}); performed at room temperature
- Pu selective de-extraction : Pu (IV) is reduced into Pu (III) by uranous nitride

  $U^{4+} + 2\,Pu^{4+} + 2\,H_2O \rightarrow UO_2^{2+} + 2\,Pu^{3+} + 4H^+$

  Pu (III) is collected into the aqueous phase
- Solvent treatment: washings and filtration to eliminate radioactive impurities leading to its degradation by radiolysis
- Purification cycles for U and Pu : one cycle for U – two are necessary for Pu

Reprocessing of nuclear fuels – Main steps

Extraction operations – PUREX process (*Plutonium Uranium Refining by Extraction*)

- Recovery rate of U and Pu: 99.88 % (La Hague factory)
- Decontamination level for U and Pu (important for their re-use): decontamination factor is defined as
  - FD = $(\text{impurities/product})_{\text{input}} / (\text{impurities/product})_{\text{output}}$
  - Experimental values: FD (U)=1.5×10^6 ; FD (Pu) = 7×10^7

- Final products: U in the U_3O_8 chemical form; Pu in the chemical form PuO_2

Reprocessing of nuclear fuels – Isotopic composition of U valuables

Isotope U	Before irradiation (Kg t^{-1} of U)	After reprocessing (10 y of cooling) (Kg t^{-1} U)	Specificity
232	0	3×10^{-6}	Irradiate
233	0	4×10^{-6}	Fissile
234	0.39	0.24	Capturing
235	40	7.45	Fissile
236	0	5.37	Capturing
238	959.61	925	Convertible in fissile ^{239}Pu

Reprocessing of nuclear fuels – Isotopic composition of Pu valuables

Isotope Pu	Before irradiation (Kg t^{-1} of U)	After reprocessing (10 y of cooling) (Kg t^{-1} U)	Specificity
238	0	0.36	Alpha emitter
239	0	6.10	fissile
240	0	2.81	Capturing
241	0	1.13	Fissile
242	0	0.90	Capturing

Reprocessing of nuclear fuels – Possible strategies

Recycling

- Fissile content of recycled matters useful but nevertheless limited in amount: re-enrichment of recycled U is mandatory
- Drawbacks due to the creation of artificial isotopes
  - Nuisance for neutronics since they absorb neutrons (severe drawback for PWR reactors)
  - Harmful for their manipulation (high radioactivity)
  - Fraction of artificial isotopes increases with burnup (and multi-recycling)
- Possible solutions
  - Isotopic separation (e.g. laser): too costly nowadays
  - Use of fast neutron reactors capable to fission all Pu isotopes: next generation of power plants (Gen 4)
- Current strategy
  - Recycled U is considered as a strategic reserve
  - Recycled Pu is used in PWR reactors as MOX fuel
  - Multi-recycling of MOX fuels under investigation since 2020

Reprocessing of nuclear fuels – Possible strategies – MOX fuel

Recycling in PWR reactors (lack of a better world)

- Neutronics perturbation since PWR were designed for regular UO_2 fuels
  - Pu isotopes absorption larger than U isotopes
  - Minimisation of the Pu charge by using an heterogeneous distribution of fissile nuclei: MOX fuel involves Pu nuclei embedded in a depleted U matrix and regular enriched UO_2
  - Single recycling (multi-recycling is hampered by the Pu degradation but considered as a possibility since 2020)
- Characteristic features of the MOX fuel (MELOX factory at Marcoule – production 100 tonnes a year):
  - Mixing of depleted UO_2 powders and recycled PuO_2 (typically from 2 to 6% of Pu)
  - Similar synthesis as for UO_2 with a special emphasis regarding homogeneity
  - Confinement of powders and protection against ^{241}Am

Reprocessing of nuclear fuels – Possible strategies – MOX fuel

Recycling in PWR reactors (lack of a better world)

- Specific distribution of MOX fuels into the reactor
  - Typically 30 % MOX; 70 % UO_2
  - Three different Pu content
  - Location of MOX fuel well defined
- MOX overview
  - Pu balance is almost zero: amount of burned Pu is almost the same as the amount of produced Pu (constant Pu stockpile)
  - Less consumption of natural U (12 % for a recycled MOX 30/70)

Reprocessing of nuclear fuels – Possible strategies – MOX fuel

Recycling in PWR reactors (lack of a better world)

- Overview of existing MOX reactors
  - France - Since 2000: 20 PWR reactors (900 MWe MOX 30/70)
  - Synthesis of 100 tons per year (corresponding to the reprocessing of 850 tons of spent irradiated UO_2)

Conditioning of reprocessed nuclear wastes

High level wastes

- Fission products (~ 5% of original U atoms)
- Vitrified ashes of fission products : almost the totality of radioactivity (except ^{236}U and Pu)
- Vitrification process
  - Drying and calcination at 1100 K of fission products (oxides) in solution (or suspended particles) in a nitric solution
  - Glass frit is added: borosilicate glass (R7T7 type)
  - Mixing of calcinated FP and are heated in an induction furnace at 1400 K: FP oxides are incorporated into the glass structure
  - Molten liquid glass is casted in a stainless steel container; after solidification a cover is welded
  - Container volume 180 L; weight 400 Kg; activity: 16×10^3 TBq $\beta\gamma$ and 230 TBq α; Thermal power : 2 KW (storage in a cooled building)
  - French production : 600 containers a year; total production 10×10^3 containers

Conditioning of reprocessed nuclear wastes

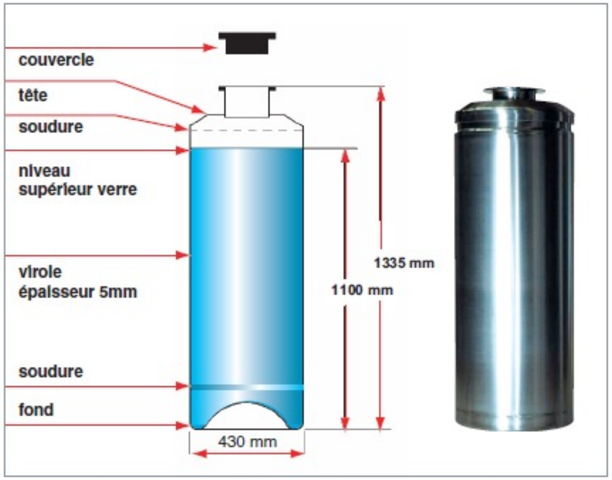
High level wastes

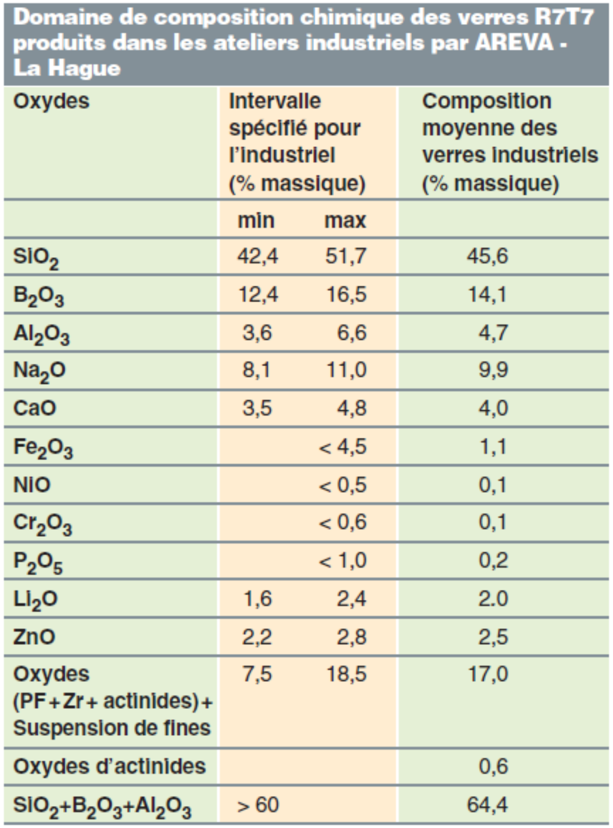
- Nuclear glass for high level nuclear wastes produced by the ORANO facility at La Hague (ex-Cogema), named after two vitrification workshops UP2-800 (R7) and UP3 (T7)
- Main elements of the glass matrix (borosilicate glass) : SiO_2, Na_2O, B_2O_3, Al_2O_3
- Able to incorporate up to 15% of nuclear wastes (fission products FP in oxide forms FP_2O_3; long-life FP ^{93}Zr, ^{99}Tc, ^{107}Pd, ^{129}I, ^{135}Cs)
- Full amount of nuclear glass (high level nuclear wastes) produced in France from the beginning of nuclear power is about 3650 m^3
  - Volume of an Olympic swimming pool is $50 \times 25 \times 3 = 3750\ m^3$
- Final geological disposal (Bure location – Grand Est district)

Conditioning of reprocessed nuclear wastes

High level wastes

- French R7T7 glass





Domaine de composition chimique des verres R7T7 produits dans les ateliers industriels par AREVA - La Hague

Oxydes	Intervalle spécifié pour l'industriel (% massique)		Composition moyenne des verres industriels (% massique)
	min	max	
SiO_2	42,4	51,7	45,6
B_2O_3	12,4	16,5	14,1
Al_2O_3	3,6	6,6	4,7
Na_2O	8,1	11,0	9,9
CaO	3,5	4,8	4,0
Fe_2O_3		< 4,5	1,1
NiO		< 0,5	0,1
Cr_2O_3		< 0,6	0,1
P_2O_5		< 1,0	0,2
Li_2O	1,6	2,4	2.0
ZnO	2,2	2,8	2,5
Oxydes (PF+Zr+ actinides)+ Suspension de fines	7,5	18,5	17,0
Oxydes d'actinides			0,6
$SiO_2+B_2O_3+Al_2O_3$	> 60		64,4

Interim storage of high level nuclear wastes

Yearly needs for interim storage (assuming 56 PWR reactors, Pu recycling in MOX, and no reprocessing of MOX fuels)

- 110 tons of MOX to store in swimming pools
- 750 containers of vitrified wastes (120 m^3 of glass)
- 1000 containers of compacted wastes (structures of reprocessed assemblies – 180 m^3)
- Wastes are stored at the La Hague site

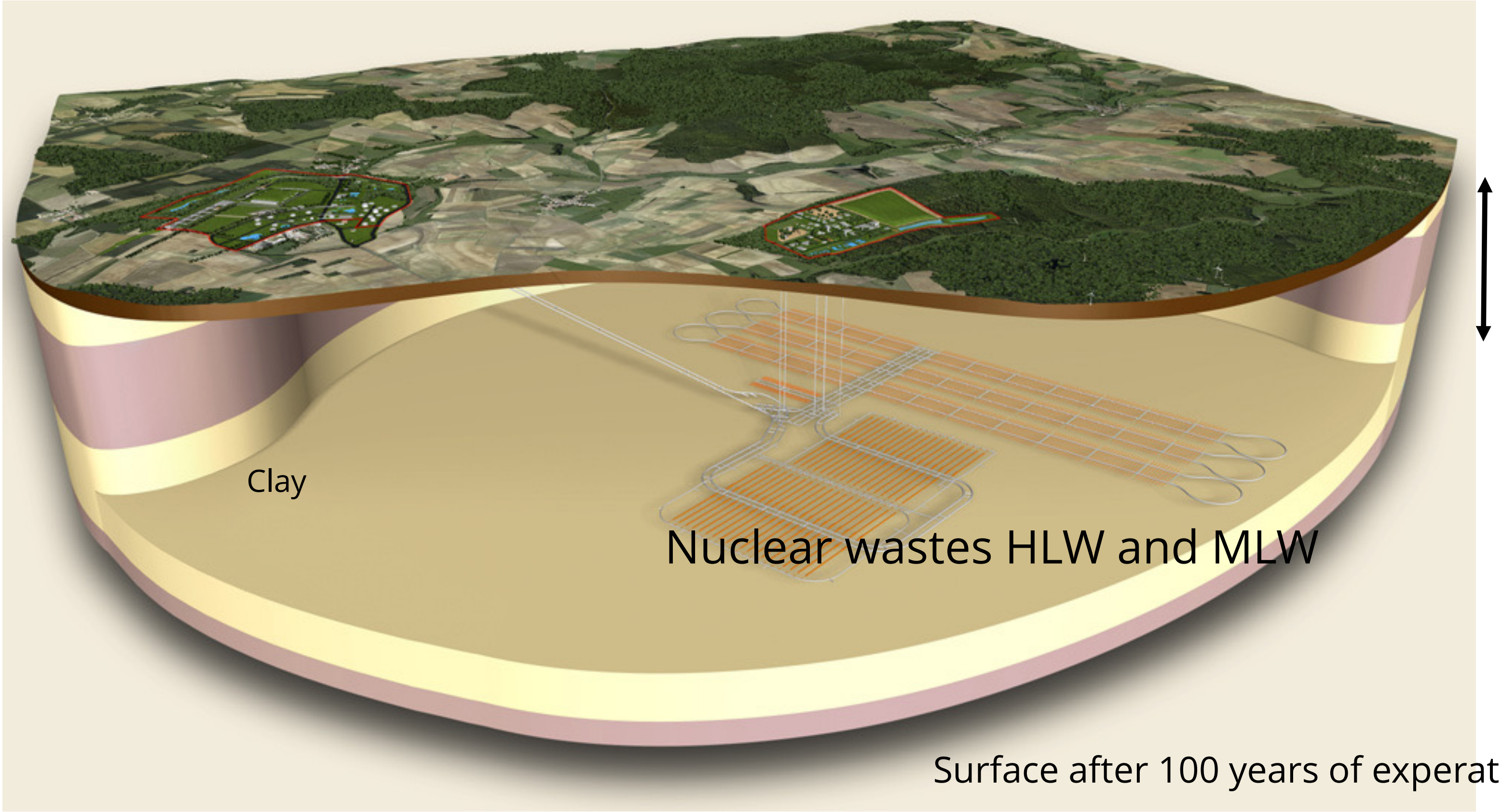
Interim storage of high level nuclear wastes

Design of interim storage locations

- Minimum lifetime 30 years (even 50 years) with a guarantee regarding the integrity of the waste package
- Waste package can be transported to another location for final disposal
- Safety criteria : confinement – criticality – thermal risks – radiolysis – handling risks
- Final fate of high level nuclear wastes is the deep underground geological storage at the Bure facility

Final disposal of high level nuclear wastes

Deep underground geological site Cigéo at Bure



Surface after 100 years of experation : 15 km^2

Loi n° 2006-739 du 28 juin 2006 « gestion durable des matières et déchets radioactifs » Stockage réversible