RDCH 702: Lecture 10 Radiochemistry in reactors

- **Readings: Radiochemistry in Light Water Reactors, Chapter 3 (on readings webpage and lecture webpage)**

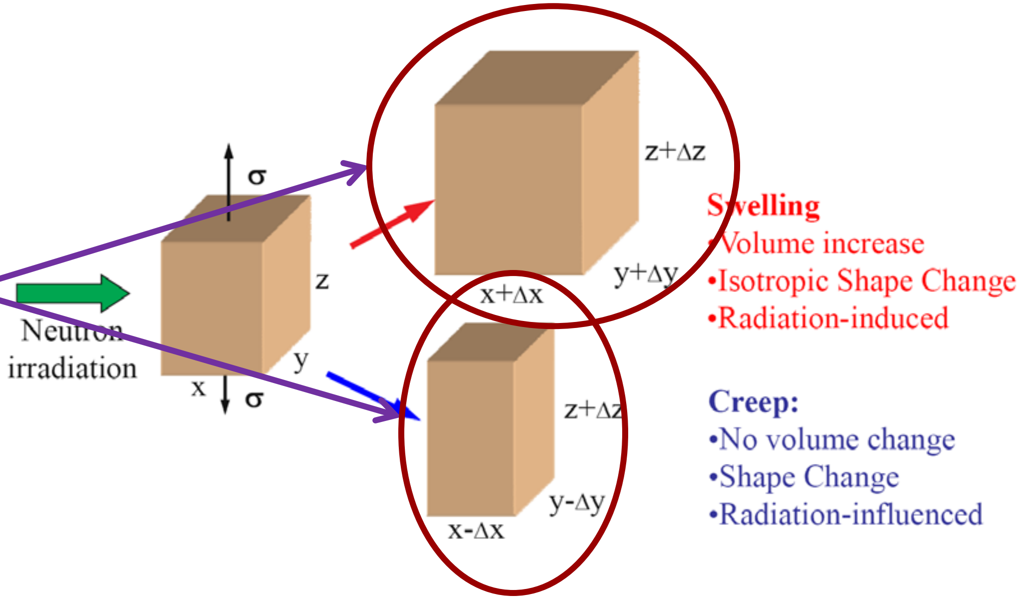
Outline

- **Speciation in irradiated fuel**
- **Utilization of resulting isotopics**
- **Fission Product Chemistry**

- **Fuel confined in reactor to fuel region**
  - **Potential for interaction with cladding material**
    - **→ Initiate stress corrosion cracking**
  - **Chemical knowledge useful in events where fuel is outside of cladding**
- **Some radionuclides generated in structural material**
  - **Neutron activation of material**
    - **→ Activation products (i.e., ^{60}Co)**

Fission process

- **Fission drives process for introducing elements into fuel**
- **Recoil length about 10 microns, diameter of 6 nm**
    - **About size of UO_2 crystal**
    - **95 % of energy into stopping power**
        - → **Remainder into lattice defects**
            - * **Radiation induced creep**
            - * **Swelling**
    - **High local temperature from fission**
        - → **3300 K in 10 nm diameter**
- **Delayed neutron fission products**
    - **0.75 % of total neutrons**
        - → **$^{137-139}I$ and $^{87-90}Br$ as examples**
- **Some neutron capture of fission products**
    - **influences effective decay constant**



Swelling
•Volume increase
•Isotropic Shape Change
•Radiation-induced

Creep:
•No volume change
•Shape Change
•Radiation-influenced

$$\lambda_{eff} = \lambda + \sigma\phi$$

Burnup

- Measure of extracted energy from fuel
  - Fraction of fuel atoms that underwent fission
    - → %FIMA (fissions per initial metal atom)
  - Actual energy released per mass of initial fuel
    - → Gigawatt-days/metric ton heavy metal (GWd/MTHM)
    - → Megawatt-days/kg heavy metal (MWd/kgHM)
    - → 1 MeV=4.45E-23 MW h
- Burnup relationship
  - Plant thermal power times days dividing by the mass of the initial fuel loading
  - Converting between percent and energy/mass by using energy released per fission event
    - → typical value is 200 MeV/fission
    - → 100 % burnup around 1000 GWd/MTHM
- Determine burnup
  - Find residual concentrations of fissile nuclides after irradiation
    - → Burnup from difference between final and initial values
    - → Need to account for neutron capture on fissile nuclides
  - Find fission product concentration in fuel
    - → Need suitable half-life
    - → Need knowledge of nuclear data
      - * cumulative fission yield, neutron capture cross section
    - → Simple analytical procedure
    - → ^{137}Cs (some migration issues) ^{142}Nd(stable isotope), ^{152}Eu are suitable fission products
  - Neutron detection also used
    - → Need to minimize ^{244}Cm due to spontaneous fission of isotope

Radionuclides in fuel

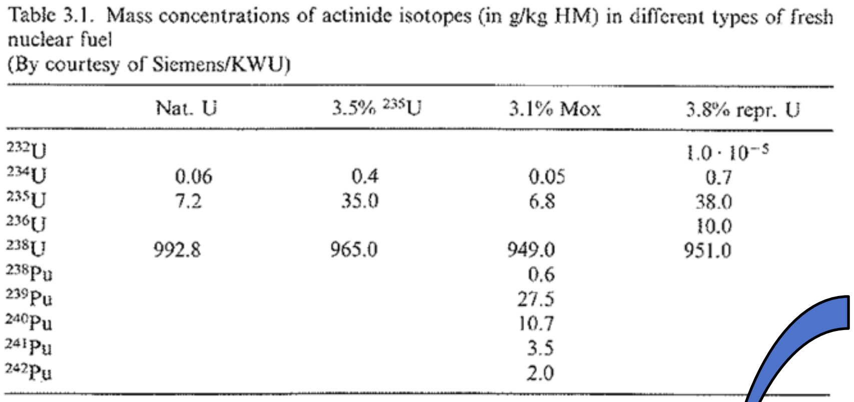


Table 3.1. Mass concentrations of actinide isotopes (in g/kg HM) in different types of fresh nuclear fuel
(By courtesy of Siemens/KWU)

	Nat. U	3.5% ^{235}U	3.1% Mox	3.8% repr. U
^{232}U				$1.0 \cdot 10^{-5}$
^{234}U	0.06	0.4	0.05	0.7
^{235}U	7.2	35.0	6.8	38.0
^{236}U				10.0
^{238}U	992.8	965.0	949.0	951.0
^{238}Pu			0.6	
^{239}Pu			27.5	
^{240}Pu			10.7	
^{241}Pu			3.5	
^{242}Pu			2.0	

- **Actual Pu isotopics in MOX fuel may vary**
  - **Activity dominated by other Pu isotopes**
  - **Ingrowth of ^{241}Am**
  - **MOX fuel fabrication in glove boxes**

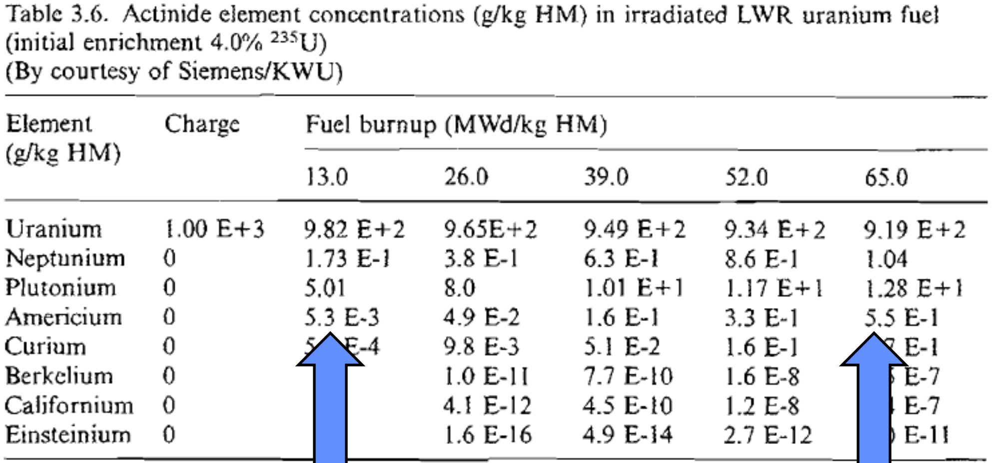


Table 3.6. Actinide element concentrations (g/kg HM) in irradiated LWR uranium fuel (initial enrichment 4.0% ^{235}U)
(By courtesy of Siemens/KWU)

Element (g/kg HM)	Charge	Fuel burnup (MWd/kg HM)				
		13.0	26.0	39.0	52.0	65.0
Uranium	1.00 E+3	9.82 E+2	9.65E+2	9.49 E+2	9.34 E+2	9.19 E+2
Neptunium	0	1.73 E-1	3.8 E-1	6.3 E-1	8.6 E-1	1.04
Plutonium	0	5.01	8.0	1.01 E+1	1.17 E+1	1.28 E+1
Americium	0	5.3 E-3	4.9 E-2	1.6 E-1	3.3 E-1	5.5 E-1
Curium	0	[illegible]	9.8 E-3	5.1 E-2	1.6 E-1	[illegible]
Berkelium	0		1.0 E-11	7.7 E-10	1.6 E-8	[illegible]
Californium	0		4.1 E-12	4.5 E-10	1.2 E-8	[illegible]
Einsteinium	0		1.6 E-16	4.9 E-14	2.7 E-12	[illegible]

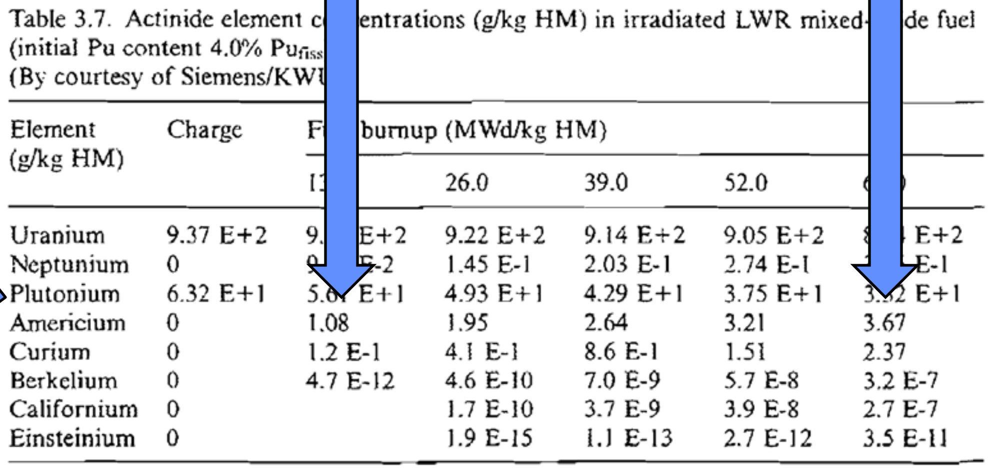


Table 3.7. Actinide element c[illegible]entrations (g/kg HM) in irradiated LWR mixed-[illegible]de fuel (initial Pu content 4.0% Pu_{fiss}[illegible]
(By courtesy of Siemens/KW[illegible]

Element (g/kg HM)	Charge	F[illegible] burnup (MWd/kg HM)				
		[illegible]	26.0	39.0	52.0	[illegible]
Uranium	9.37 E+2	[illegible]	9.22 E+2	9.14 E+2	9.05 E+2	[illegible]
Neptunium	0	[illegible]	1.45 E-1	2.03 E-1	2.74 E-1	[illegible]
Plutonium	6.32 E+1	[illegible]	4.93 E+1	4.29 E+1	3.75 E+1	[illegible]
Americium	0	1.08	1.95	2.64	3.21	3.67
Curium	0	1.2 E-1	4.1 E-1	8.6 E-1	1.51	2.37
Berkelium	0	4.7 E-12	4.6 E-10	7.0 E-9	5.7 E-8	3.2 E-7
Californium	0		1.7 E-10	3.7 E-9	3.9 E-8	2.7 E-7
Einsteinium	0		1.9 E-15	1.1 E-13	2.7 E-12	3.5 E-11

Fuel variation during irradiation

- Chemical composition of fuel
  - Higher concentrations of Ru, Rh, and Pd in Pu fuel
- Radionuclide inventory
- Pellet structure
- Total activity of fuel effected by saturation
  - Tends to reach maximum
- Radionuclide fuel distribution studied
  - Fission gas release
  - Axial distribution by gamma scanning
- Radial distribution to evaluate flux

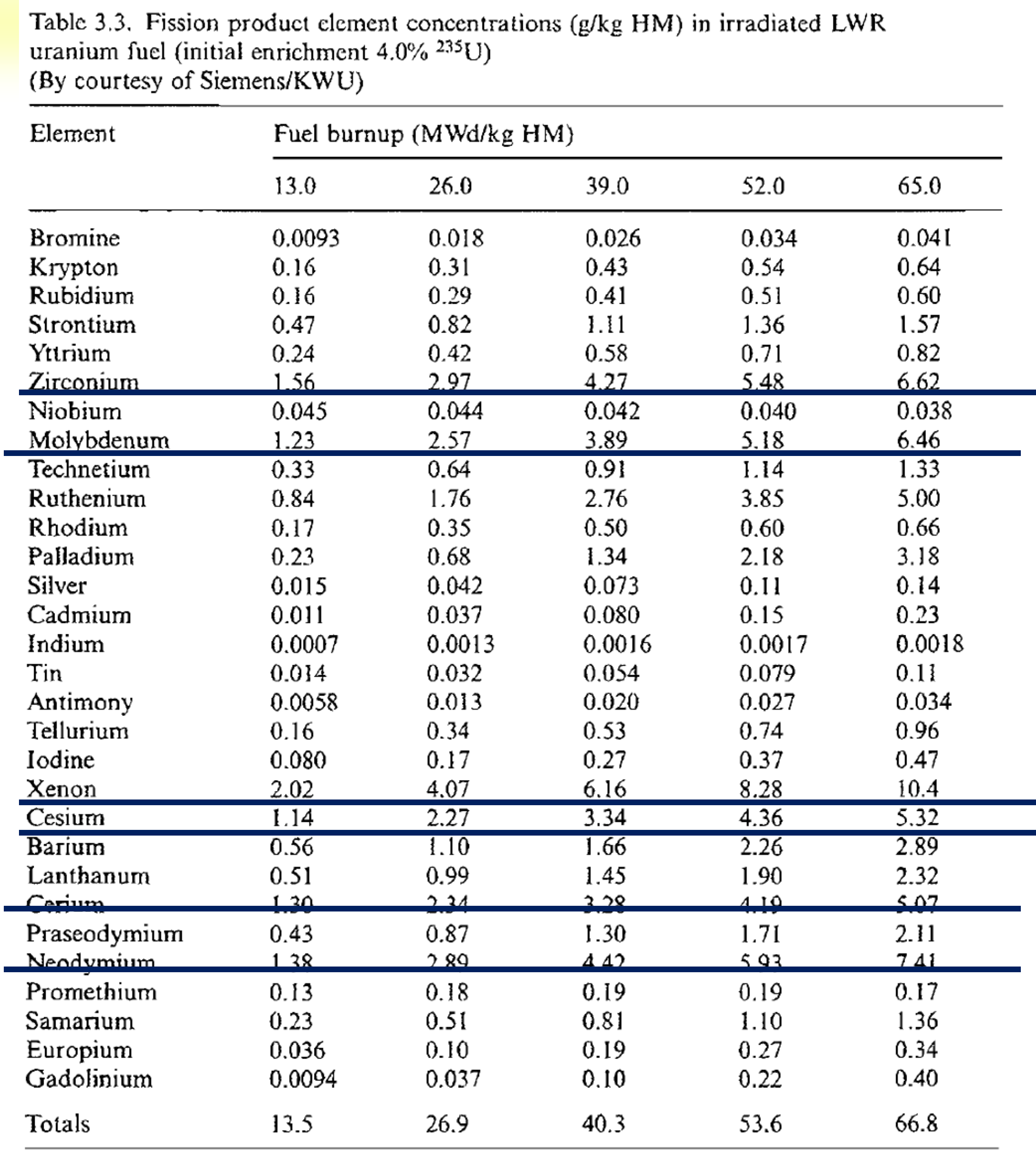


Table 3.3. Fission product element concentrations (g/kg HM) in irradiated LWR uranium fuel (initial enrichment 4.0% ^{235}U)
(By courtesy of Siemens/KWU)

Element	Fuel burnup (MWd/kg HM)				
	13.0	26.0	39.0	52.0	65.0
Bromine	0.0093	0.018	0.026	0.034	0.041
Krypton	0.16	0.31	0.43	0.54	0.64
Rubidium	0.16	0.29	0.41	0.51	0.60
Strontium	0.47	0.82	1.11	1.36	1.57
Yttrium	0.24	0.42	0.58	0.71	0.82
Zirconium	1.56	2.97	4.27	5.48	6.62
Niobium	0.045	0.044	0.042	0.040	0.038
Molybdenum	1.23	2.57	3.89	5.18	6.46
Technetium	0.33	0.64	0.91	1.14	1.33
Ruthenium	0.84	1.76	2.76	3.85	5.00
Rhodium	0.17	0.35	0.50	0.60	0.66
Palladium	0.23	0.68	1.34	2.18	3.18
Silver	0.015	0.042	0.073	0.11	0.14
Cadmium	0.011	0.037	0.080	0.15	0.23
Indium	0.0007	0.0013	0.0016	0.0017	0.0018
Tin	0.014	0.032	0.054	0.079	0.11
Antimony	0.0058	0.013	0.020	0.027	0.034
Tellurium	0.16	0.34	0.53	0.74	0.96
Iodine	0.080	0.17	0.27	0.37	0.47
Xenon	2.02	4.07	6.16	8.28	10.4
Cesium	1.14	2.27	3.34	4.36	5.32
Barium	0.56	1.10	1.66	2.26	2.89
Lanthanum	0.51	0.99	1.45	1.90	2.32
Cerium	1.30	2.34	3.28	4.19	5.07
Praseodymium	0.43	0.87	1.30	1.71	2.11
Neodymium	1.38	2.89	4.42	5.93	7.41
Promethium	0.13	0.18	0.19	0.19	0.17
Samarium	0.23	0.51	0.81	1.10	1.36
Europium	0.036	0.10	0.19	0.27	0.34
Gadolinium	0.0094	0.037	0.10	0.22	0.40
Totals	13.5	26.9	40.3	53.6	66.8

Distribution in fuel

- **Axial fission product distribution corresponds very closely to the time-averaged neutron flux distribution**
  - **PWR activity level in the middle**
  - **Activity minima from neutron shielding effect of spacer grids**
    - **→ local decrease in fission rates**
  - **Fuel density effects**
    - **→ Dishing at end of fuel**
    - **→ Disappear due to fuel swelling**
  - **BWR shows asymmetric distribution**
    - **→ Control rod positions**

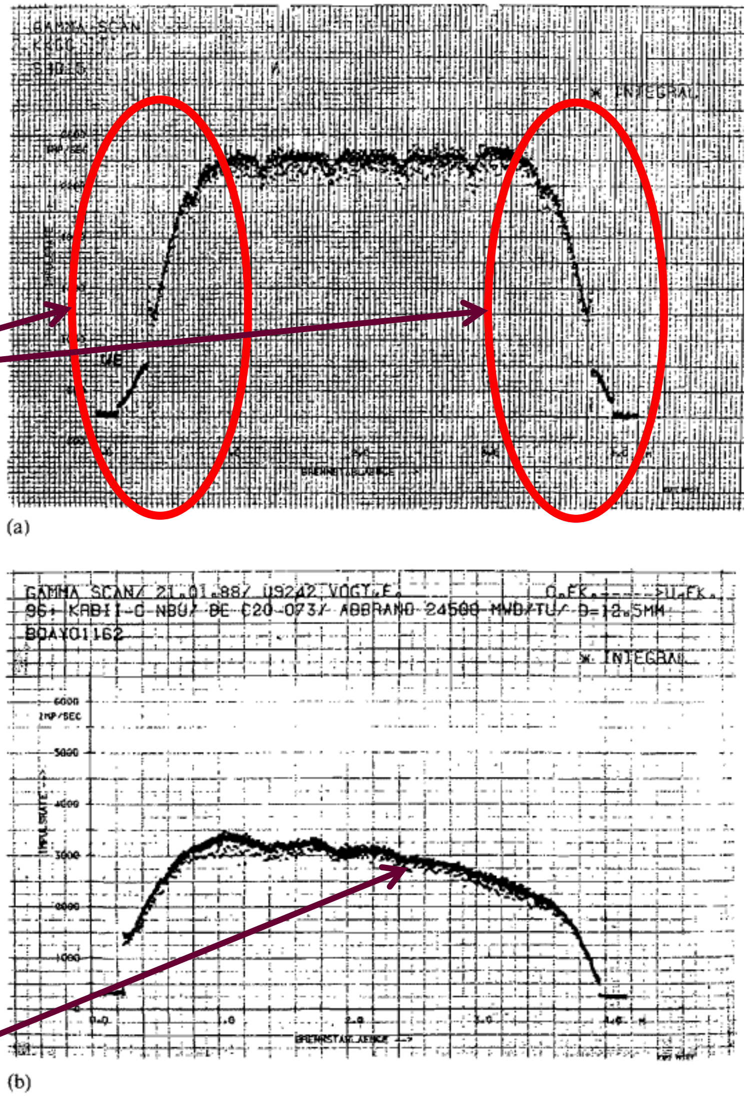
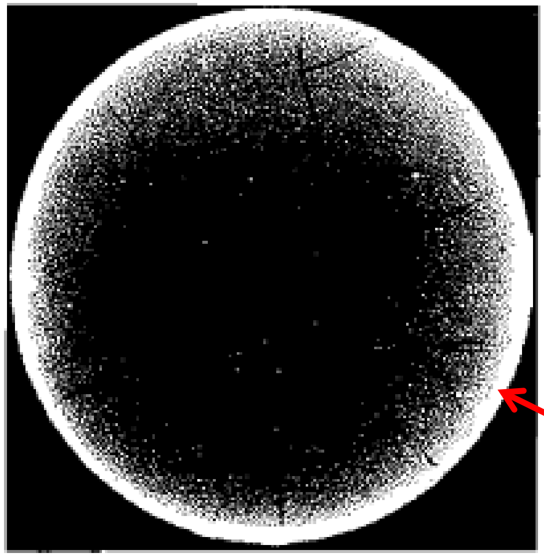
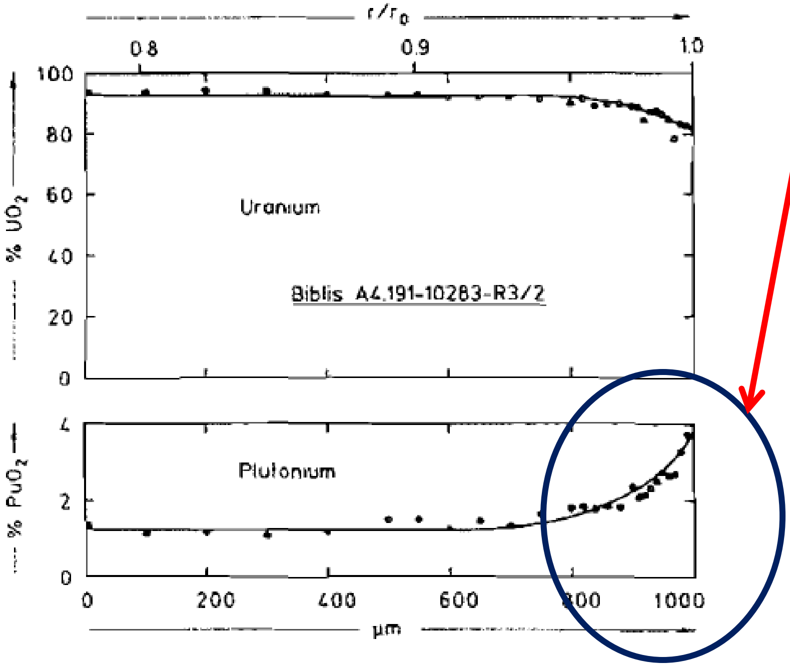


Figure 3.6. Axial gross gamma scans of high-burnup fuel rods
a) PWR fuel rod; b) BWR fuel rod
(By courtesy of Siemens/KWU)

Distribution in Fuel



Transuranics on fuel rim



- **Radial distribution of fission products mainly governed by thermal neutron flux profile**
- **Higher Pu concentration in outer zone of fuel**
  - **Epithermal neutron capture on ^{238}U**
  - **Small influence of thermal migration on Cs**
    - → **Gaseous and volatile fission products**
    - → **Influence by fuel initial composition (O to M ratio)**

Distribution in Fuel

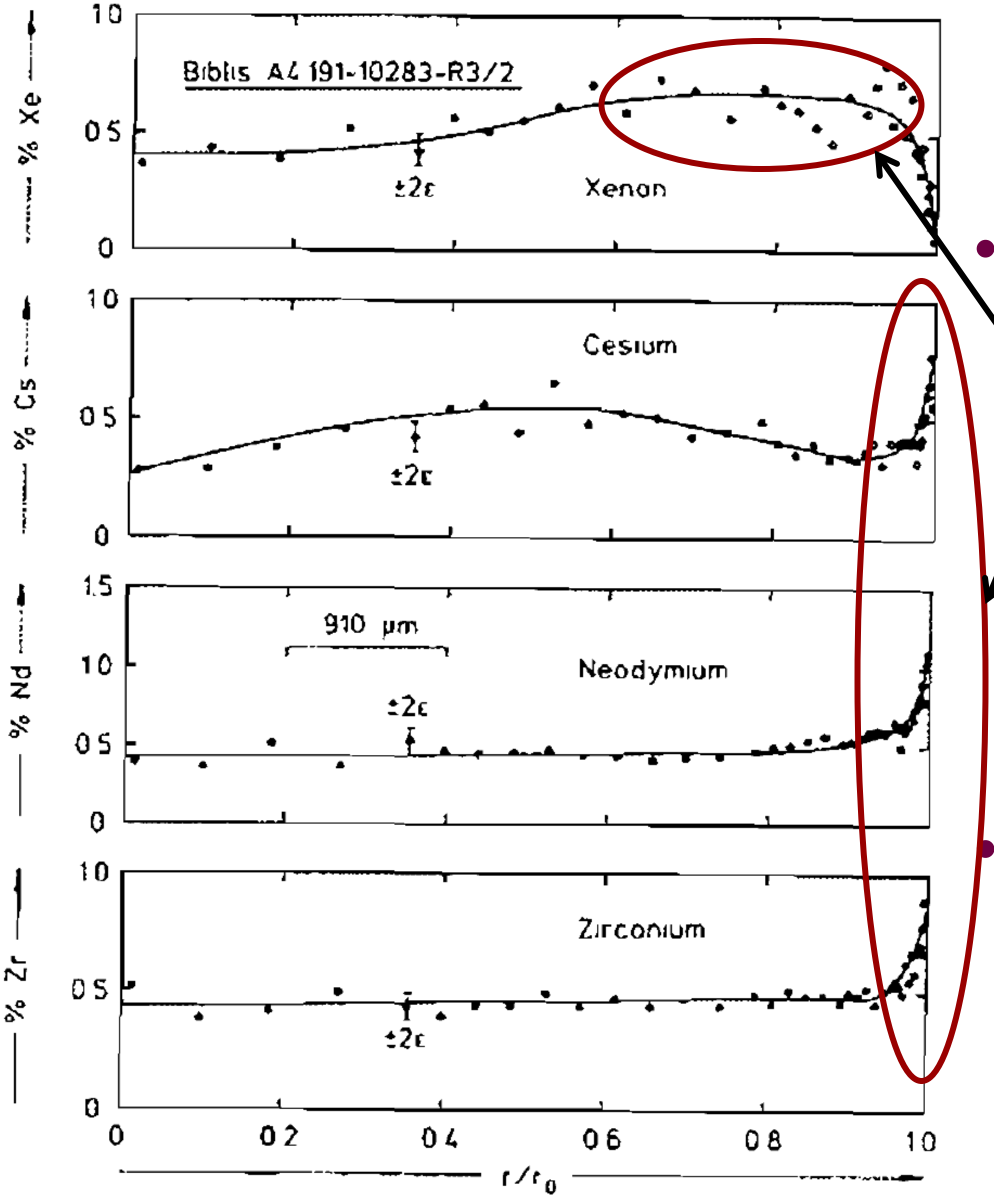


Figure 3.9. Fission product distribution as a function of the relative fuel pellet radius in a LWR high-burnup oxide fuel
(Kleykamp, 1990 a)

- Increased Pu concentration on rim leads to increased fission product density
  - Xe behavior influenced by bubble gas location
- Consumption of burnable poison
  - Gd isotopes 157 and 155 depleted in outer zone

Distribution in fuel: Thermal behavior

- Mainly affects gaseous and volatile fission products
  - linear heat rating
  - pellet temperatures during reactor operation
  - stoichiometry of fuel
- Halogens and alkali elements
  - Cs and I volatility
    - → High fission yields
    - → Enhanced mobility
  - Can be treated similarly
    - → different chemical behavior limited in fuel behavior

Iodine and Cs

- CsI added to UO_2
    - Both elements have same maximum location at 1000 °C
    - Behavior as CsI
- UO_{2+x}
    - Iodine property changes, mobility to lower temperature regions
        - → Elemental I_2 rather than I^-
- Formation in range of x to 0.02
- No change in Cs chemistry
    - remains monovalent
- release of cesium and iodine from fuel at 1100 to 1300 K
    - Increases with temperature

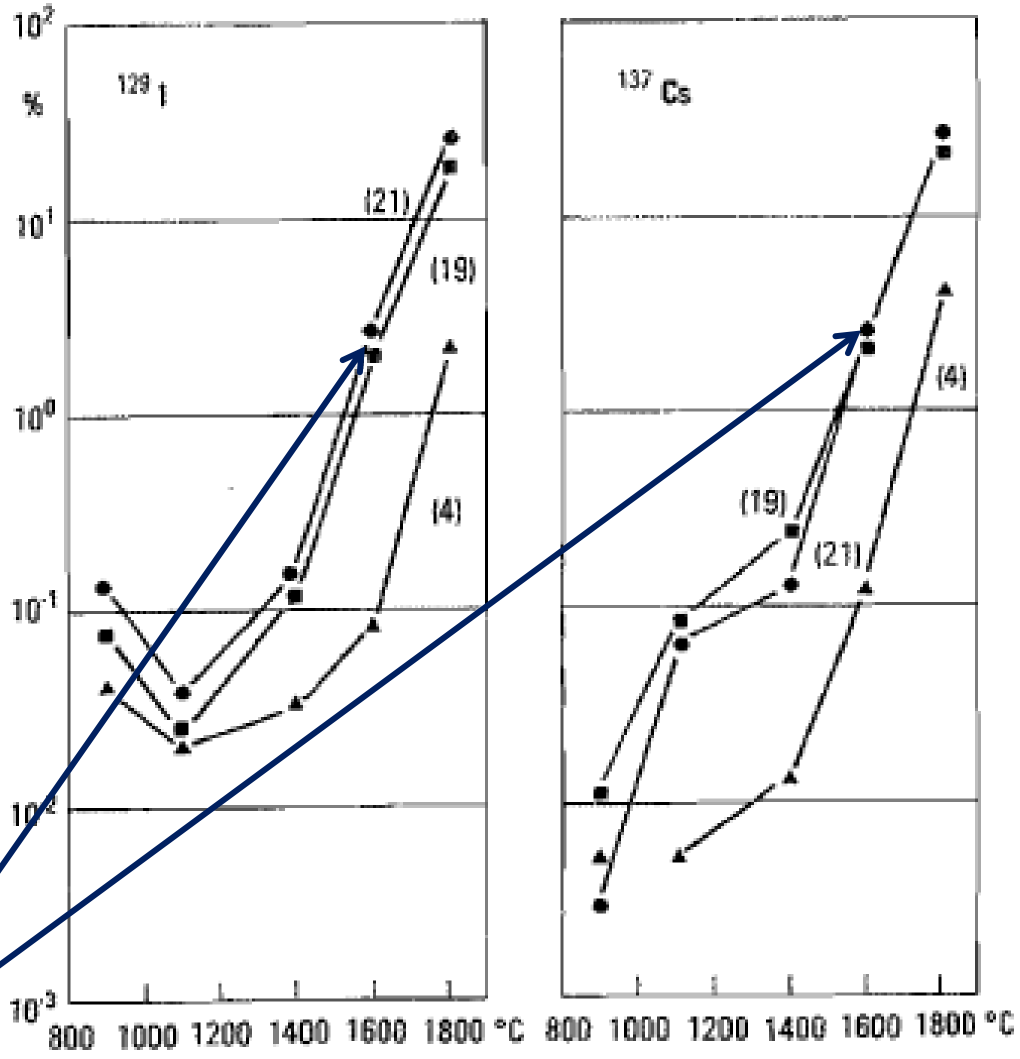


Figure 3.18. Iodine and cesium exhalation from irradiated UO_2 fuel (Sample 4: burnup 11 MWd/kg U; samples 19 and 21: 33 MWd/kg U)

Iodine and Cs

- Cs and iodine release rates increase with increasing temperature
    - 2100 K largest fraction released after 60 seconds
- Both elements released at significantly faster rate from higher-burnup fuel
    - Different release mechanism
- Attributed to fission product atoms which already migrated to grain boundaries
    - UO_2 lattice difficulty in incorporating large atomic radii ions

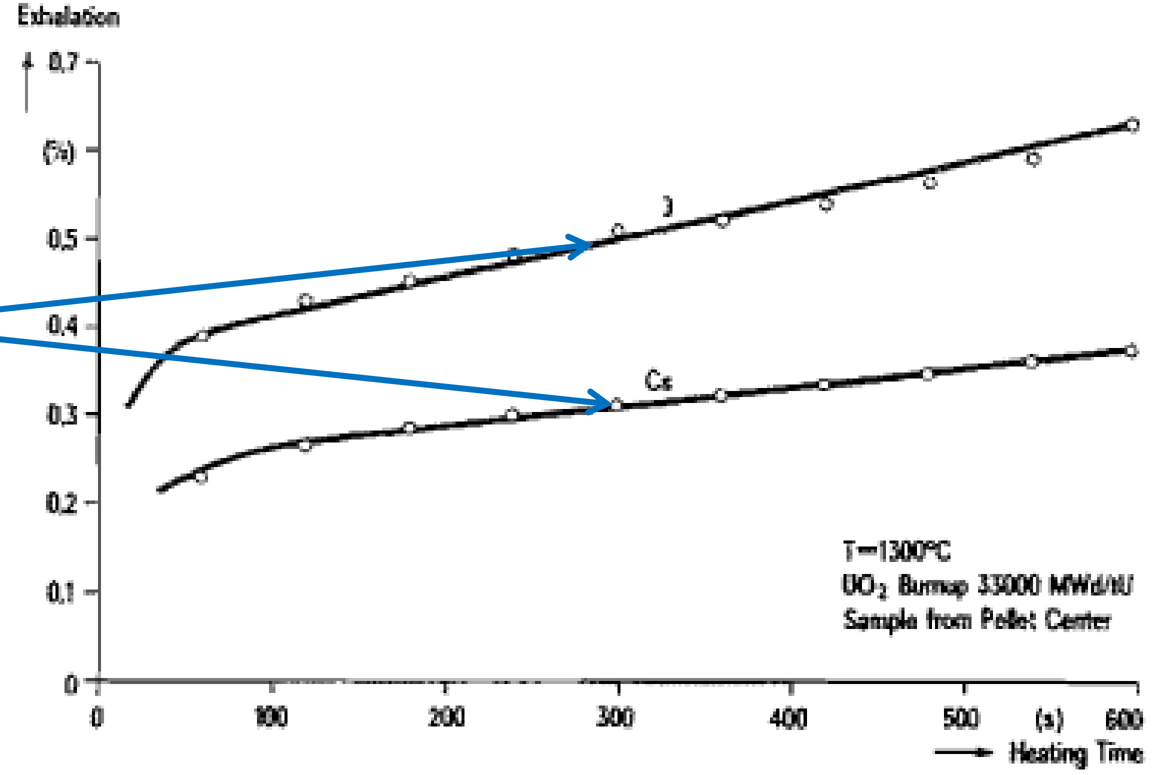
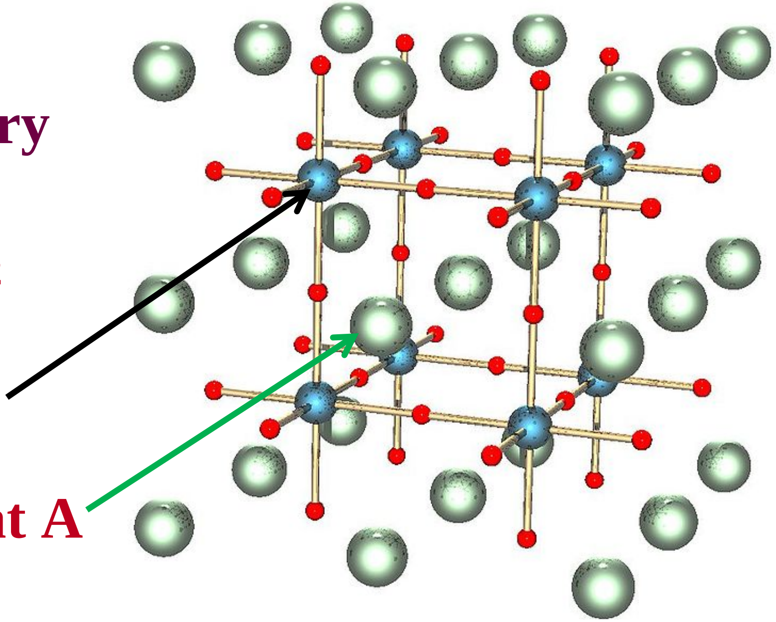


Figure 3.19. Iodine and cesium exhalation from irradiated UO_2 fuel as a function of heating time

Perovskite phase ($A^{2+}B^{4+}O_3$)

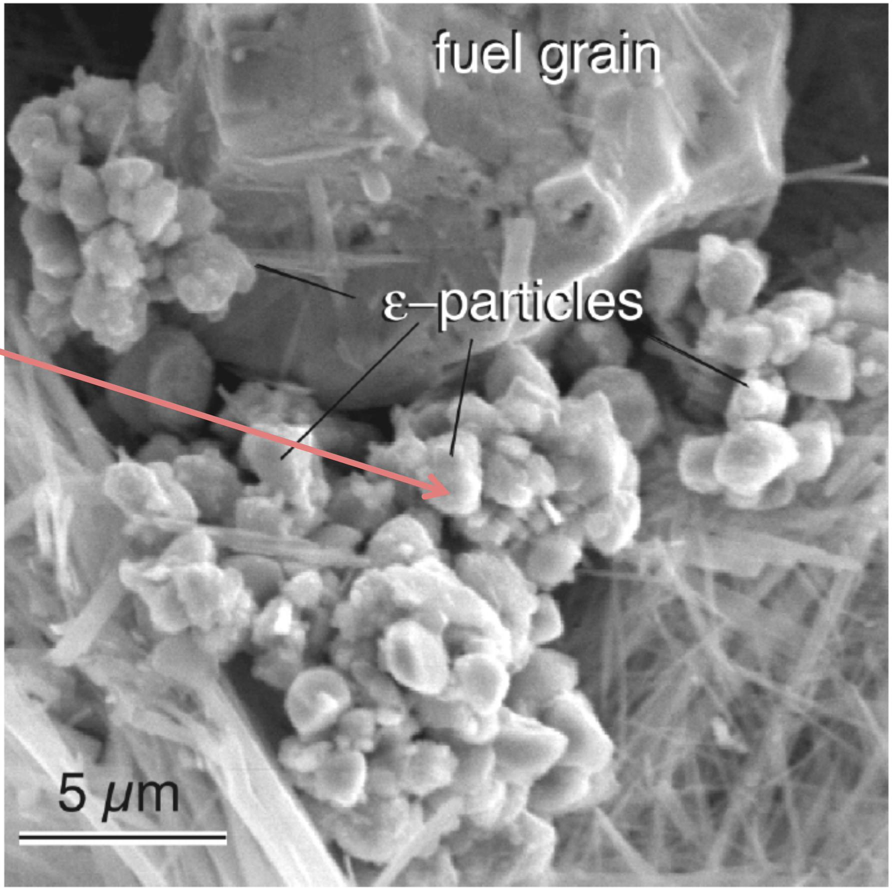
- Most fission products homogeneously distributed in UO_2 matrix
  - Solid solution formation or relatively low concentration of fission products
- With increasing fission product concentration formation of secondary phases possible
  - Exceed solubility limits in UO_2
- Perovskite identified oxide phase
  - B site: U, Pu, Zr, Mo, and Lanthanides
  - Mono- and divalent elements at A
    - → Ba, Sr, Cs
- Mechanism of formation
  - Sr and Zr form phases initially
  - Lanthanides added at high burnup



Epsilon phase

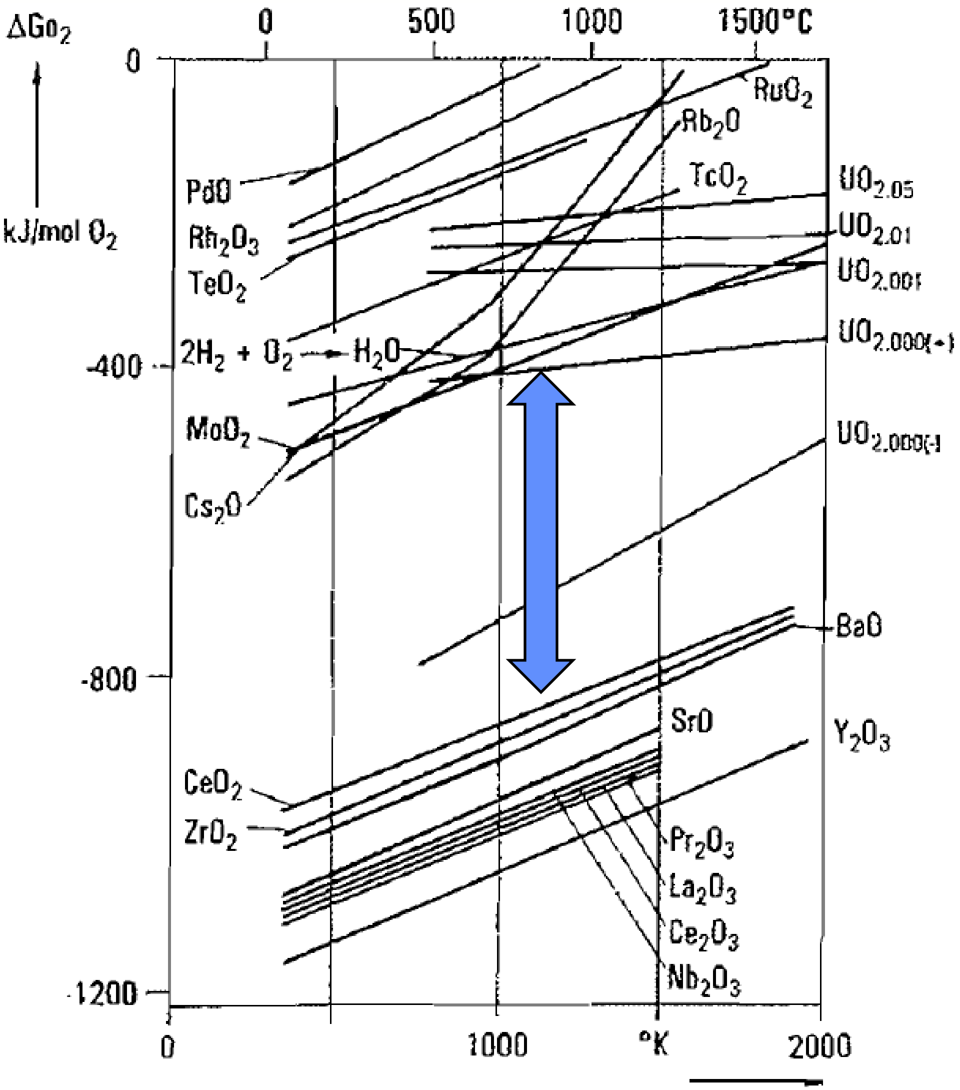
- Metallic phase of fission products in fuel
    - Mo (24-43 wt %)
    - Tc (8-16 wt %)
    - Ru (27-52 wt %)
    - Rh (4-10 wt %)
    - Pd (4-10 wt %)

      → Metal above tend to not forms oxides
- Grain sizes around 1 micron
- Concentration nearly linear with fuel burnup
    - 5 g/kg at 10 MWd/kg U
    - 15 g/kg at 40 MWd/kg U



Epsilon Phase

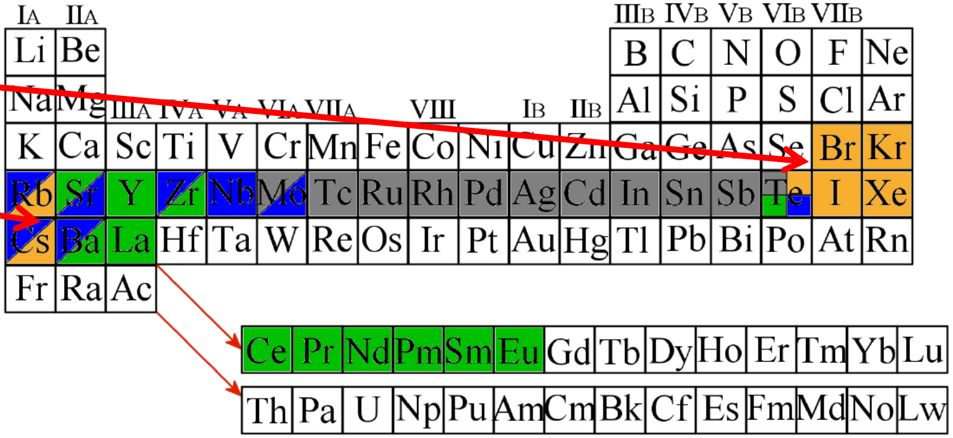
- **Formation of metallic phase promoted by higher linear heat**
  - **high Pd concentrations (20 wt %) indicate a relatively low fuel temperature**
  - **Mo behavior controlled by oxygen potential**
    - **→ High metallic Mo indicates O:M of 2**
    - **→ O:M above 2, more Mo in UO_2 lattice**



Relative partial molar Gibbs free energy of oxygen of fission product oxides and UO_2

Grouping fission product and actinide behavior

- Experiments performed between 1450 °C and 1825 °C
    - trace-irradiated UO_2 fuel material
    - Limit formation of fission products compounds
- 4 categories
- Elements with highest electronegativities have highest mobilities
    - Te, I
- Low valent cations and low fuel solubility
    - Cs, Ba
- Neutral species with low solubility
    - Xe, Ru, Tc
    - Similar behavior to low valent cations
    - (xenon, ruthenium,
- polyvalent elements were not released from fuel
    - Nd, La, Zr, Np
- Ions with high charges remain in UO_2
- Neutral atoms or monovalent fission products are mobile
    - Evident at higher temperatures
        - → higher fuel rod heat ratings
        - → accident conditions



Orange: volatile fission products

Grey: metallic precipitates

Blue: oxide precipitates

Green: solid solution

Review

- How is uranium chemistry linked with chemistry in fuel
- What are the main oxidation states of the fission products and actinides in fuel
- What drives the speciation of actinides and fission products in fuel
- How is volatility linked with fission product chemistry
- What are general trends in fission product chemistry

Questions

1. What drives the speciation of actinides and fission products in spent nuclear fuel?
2. What would be the difference between oxide and metallic fuel?
3. Why do the metallic phases form in oxide fuel
4. How is the behavior of Tc in fuel related to the U:O stoichiometry?

PDF Quiz and Blog

- **Final PDF quiz**
    - **PDF quiz 10**
- **Provide comments in blog**