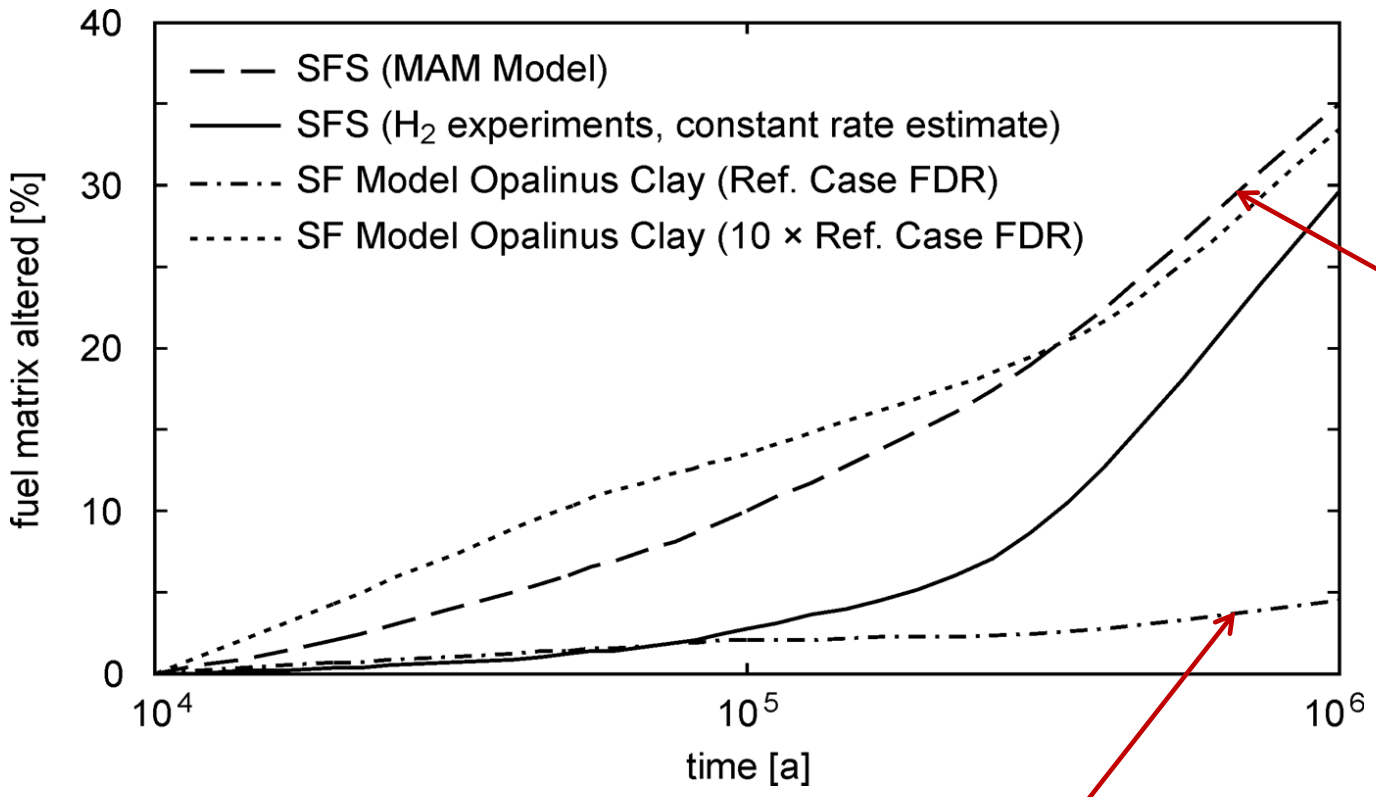
Potential Activities at PSI (NES) for a prospective EU-Project on Spent Fuel Dissolution

E. Curti, D. Kulik
Laboratory for Waste Management (LES), Paul Scherrer Institut

N. Diomidis, I. Gaus
National Cooperative for the Disposal of Radioactive Waste (Nagra)

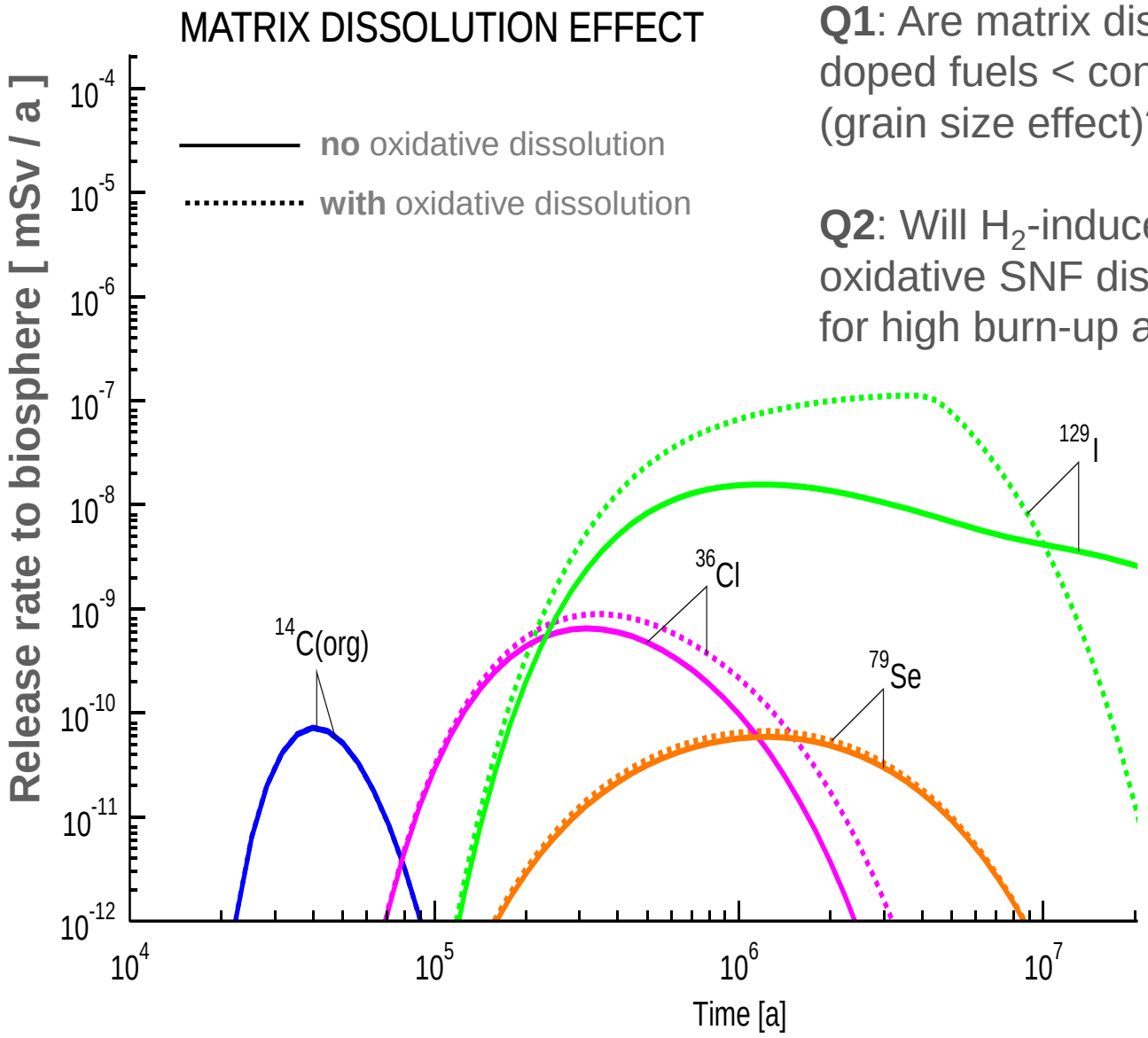
Impact of SNF dissolution in PA



MAM model
(oxidative SNF dissolution)

Current model
(H_2 suppresses oxidative SNF dissolution)

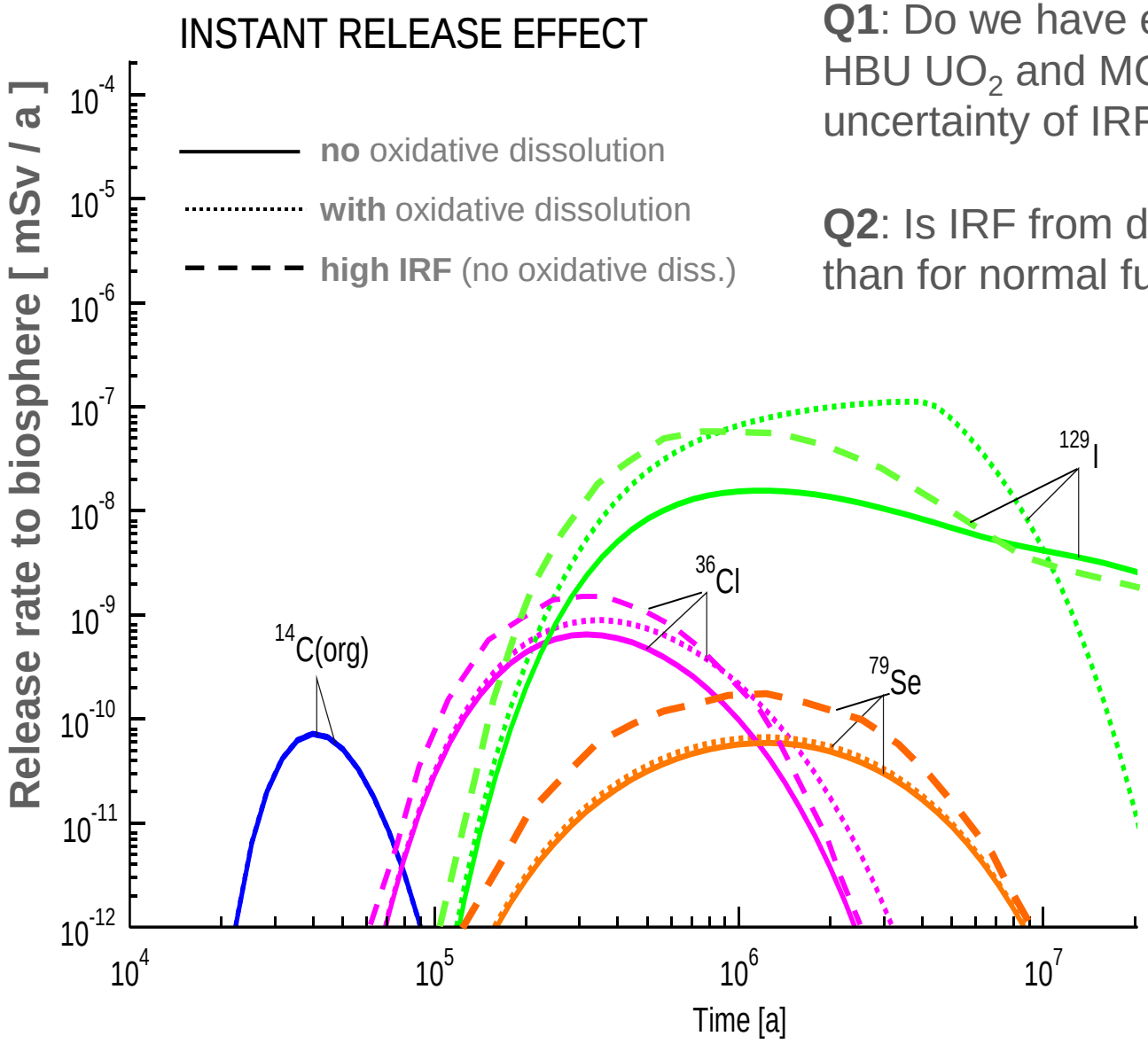
PA results “Project Opalinus Clay” (2002)



Q1: Are matrix dissolution rates of doped fuels < conventional fuels (grain size effect)?

Q2: Will H_2-induced suppression of oxidative SNF dissolution work also for high burn-up and MOX fuels?

PA results “Project Opalinus Clay” (2002)



Q1: Do we have enough data on HBU UO_2 and MOX fuel (to reduce uncertainty of IRF values)?

Q2: Is IRF from doped fuel lower than for normal fuel?

Instant Release Fractions 2002 => 2014

	IRF (%) – Opalinus Clay project (2002)		IRF (%) – SGT E2 (2014)
	Reference	Conservative	Range (fuel type)
^{14}C	10	10	10
^{36}Cl	10	26	5.4 – 48*
^{79}Se	3	17	0.2#
^{129}I	4	26	5.8 – 20*
^{135}Cs	4	26	5.8 – 13.2*

***** Maximum values: MOX fuel
# ^{79}Se value based on FIRST-Nuclides

- FIRST Nuclides data allowed differentiation of IRF-values for different types of fuels
- Large uncertainties with regard to MOX fuels
- Little/no IRF data for ^{36}Cl / ^{14}C => still very conservative values need to be used

What PSI can offer… (I)

- PSI hot-laboratory (HL) has infrastructure to perform experiments with spent nuclear fuel (SNF)
- Aqueous leaching experiments on conventional UO_2 and MOX SNF already performed in earlier projects (GAP, FIRST-Nuclides)
- HL infrastructure has currently some limitations, specifically: **No** SNF leaching experiments under **reducing conditions** possible
- Due to extremely **high costs of transfer** from the NPP-facilities, only already available in-house SNF samples could be studied.
  => non-doped & doped UO_2 and MOX fuels from Swiss NPPs.

What PSI can offer… (II)

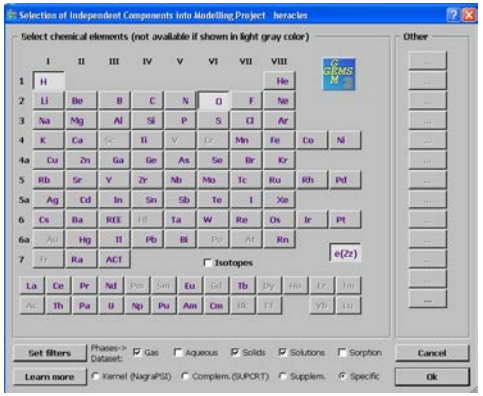
- PSI (LES) has the capability to conduct theoretical thermodynamic studies on SNF using…

GEMS-PSI

Gibbs Energy Minimization software

HERACLES

high-T database for nuclear fuels (in-reactor conditions)



PSI-Nagra 12/07

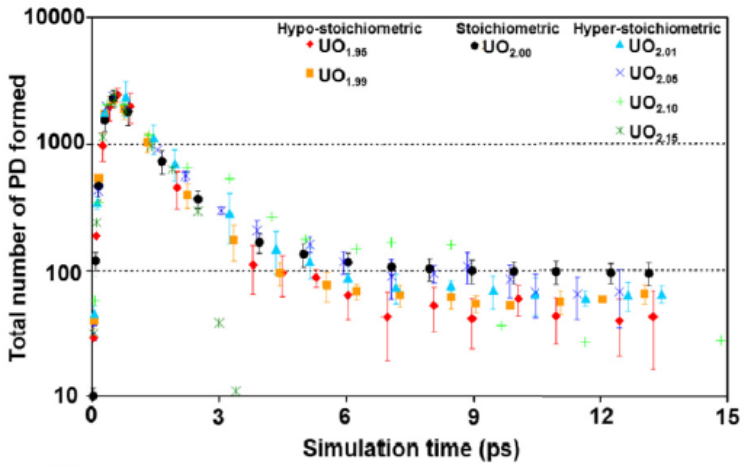
low-T database for aqueous environments (repository conditions)

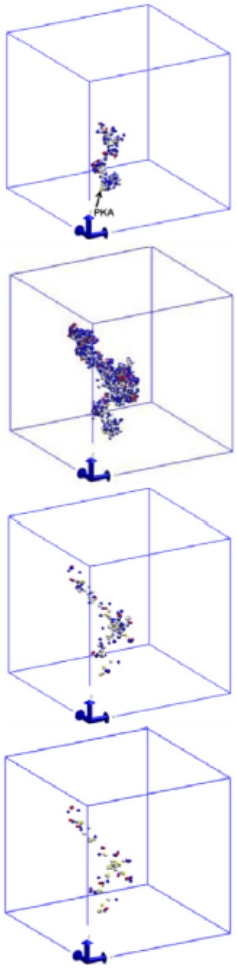
Properties of 340 condensed compounds and 290 gaseous species of actinides/FPs. Data traceable to original publications

Properties of aqueous species and solid phases. Most actinide and FP data critically reviewed (Documentation available)

What PSI can offer… (III)

- PSI (LES/LRS) has know-how in the field of molecular dynamics (including *ab initio* calculations), specifically on UO_2





(b) 0.15 ps ballistic phase

(c) 0.5 ps peak damage

(d) 3.95 ps recombination phase

(e) 13.15 ps persistent damage

Nguyen-Happy and Krack (2014) *Progr. Nucl. Energy*, 72, 38-43:

Investigation of the influence of off-stoichiometry on the radiation damage evolution in uranium dioxide

Potential PSI contributions: experimental work

Aqueous leaching of spent fuel samples:

- under air
- no added materials

⇒ FIAP as f(leaching time)
= increase IRF database

Materials currently available in our HL:

- Cr-oxide doped UO_2 fuel
- MOX fuel
- pure cladding samples
  => completion of FIRST-Nuclides

Potential PSI contributions: theoretical work

- Thermodynamic modelling of UO_2 fuel (in-reactor or dry storage conditions)

  ⇒ Oxygen potential as f($UO_{2\pm x}$, FPs, dopants)

  ⇒ Primary oxidation state of redox-sensitive FPs

  ⇒ FPs and dopants in solid solutions or pure phases

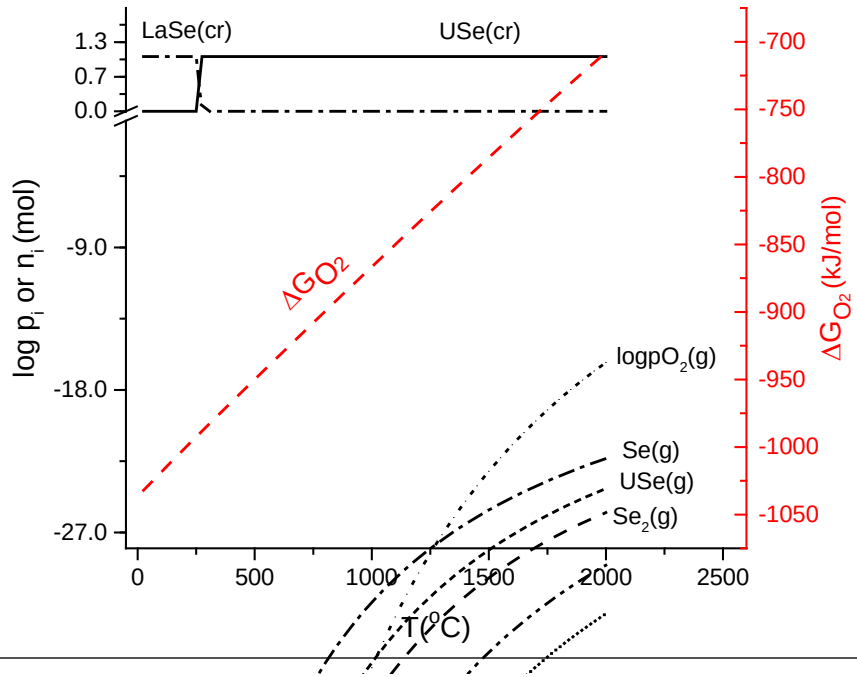
Test calculation: GEMS –PSI/ HERACLES, no solid solutions, LWR UO2 fuel model inventory

Recipe Input

	Property	Name	Quantity	Units
1	xd_	UO2	3420	M
2	bi_	Ar	14.78	M
3	bi_	Ba	28.7	M
4	bi_	Ce	26.7	M
5	bi_	Cs	21.5	M
6	bi_	I	2.86	M
7	bi_	La	13.7	M
8	bi_	Mo	55.8	M
9	bi_	O	300.55	M
10	bi_	Pd	24.2	M
11	bi_	Rb	6.47	M
12	bi_	Ru	37.1	M
13	bi_	Se	1.06	M
14	bi_	Sr	8.54	M
15	bi_	Te	6.28	M
16	bi_	Zr	66.3	M

⇐ ΣO = ΣFP

Results: Se speciation & oxygen potential



Potential PSI contributions: theoretical work

- Why should we carry out advanced thermodynamic calculations to determine the oxygen potential?

Ozrin (2011), *Journal of Nuclear Materials* 419 (2011) 371–377:
"The oxidation state of urania is one of the most important chemical properties of nuclear fuel during irradiation because of significant influence of the oxygen stoichiometry of fuel on the basic diffusion controlled processes such as grain growth [1], creep, fission gas release [1–3], the thermal conductivity [4] and the ***chemical state*** *and hence* ***behavior of the fission products*** *(FP) [5]"*

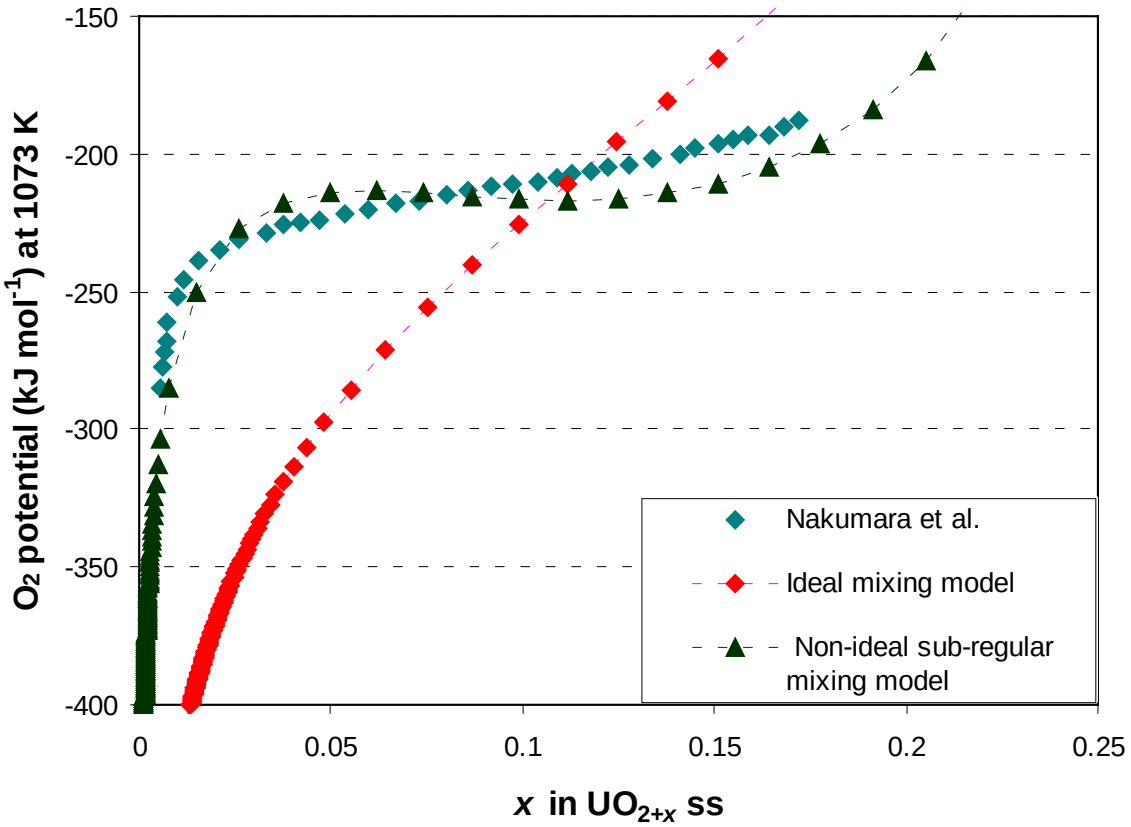
⇧

Leachability of FPs under repository conditions

Calculations can be checked against experimentally determined ΔGO_2
=> **It would be nice to have ΔGO_2 measurements on well-characterized SNF in the framework of the proposed project**

Example of SS calculations

Experimental and calculated oxygen potentials for ideal and non-ideal UO_{2+x} solid solution at 1073 K (Van Laar model)



from:

Poonoosamy et al. 2011
TM-46-11-07
Paul Scherrer Institut

and

Degueldre et al. 2014
J. Phys. Chem. Solids
75, 358-365

What PSI could do (thermodynamics of SNF)

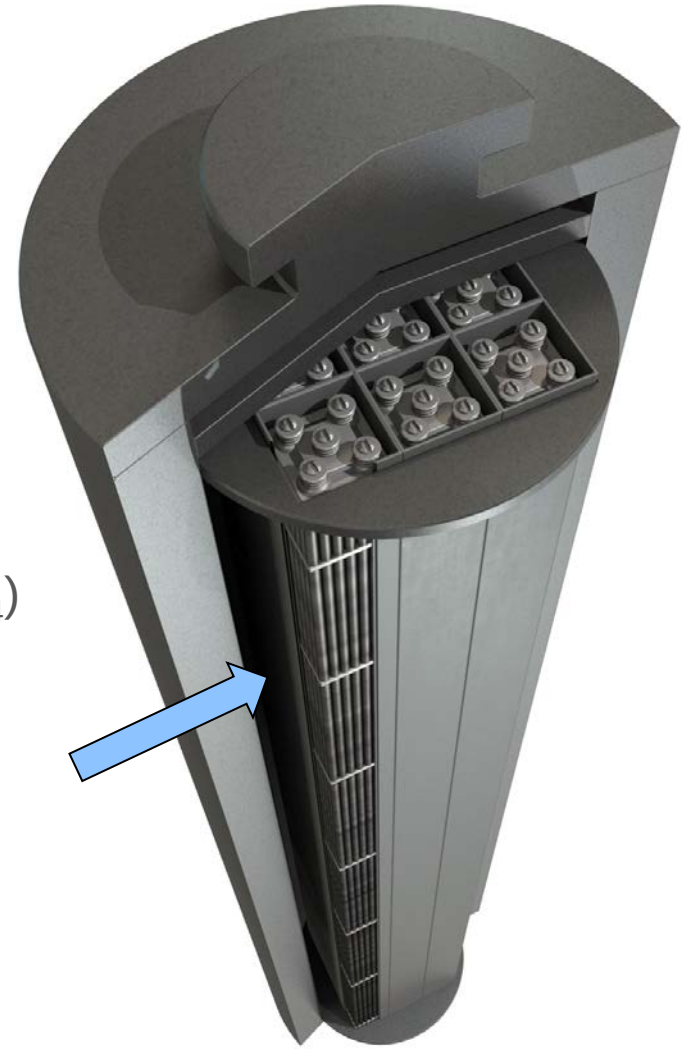
- Extend calculations to full SNF system
  - effect of dopants (Cr/Al) on ΔGO_2
  - effect of redox-sensitive FPs (e.g. Mo) on ΔGO_2
  - effect of oxygen uptake by Zircaloy (rim region)
- Improve SS models
  - Van Laar model => sublattice model for $UO_{2\pm x}$
  - include specific FPs in solid solution models (e.g. ^{79}Se in UO_{2+x} multicomponent SS)
- Benchmarks with Open CALPHAD

What PSI could do (thermodynamics of SNF)

After canister failure:
- Pore water intrusion in voids
- Very slow Zircaloy dissolution
- Slow SNF matrix dissolution
- Partially corroded metal canister (Fe^0 + Fe_3O_4)

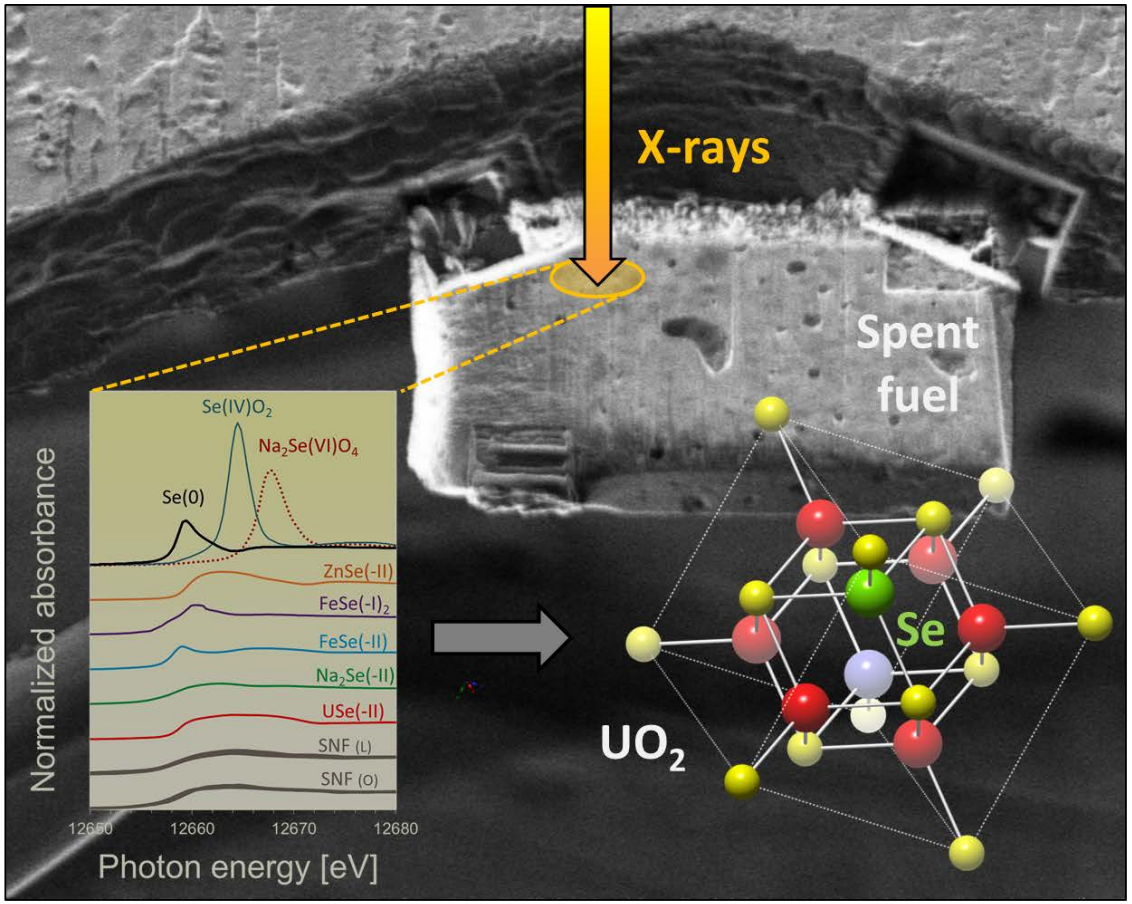
Calculate FP/An speciation assuming:
- Equilibrium SNF/canister/cladding
- Slowly dissolving SNF (partial equilibrium)
- Solid solutions in secondary phases (Ni in Fe_3O_4)
- Site-specific conditions (pore water, materials)

Results
- Radionuclide speciation in water and solids as a function of reaction progress
- Radionuclide solubility limits **inside canister**



Potential PSI contributions: theoretical work

Molecular dynamics calculations: Atomic-scale environment of ^{79}Se in SNF



FIRST-Nuclides result:
XAS data on SNF indicate ^{79}Se is trapped as Se(-II) in oxygen sites of UO_2 lattice.

Can this result be consolidated by *ab initio* molecular dynamics?

Curti et al. (2015) *Environ. Sci.: Processes & Impacts*, **17**, 1760-68

Potential PSI contributions

- Assuming a budget similar to that granted to us in FIRST-Nuclides, we could accomplish only one of the two proposed tasks (experimental **or** theoretical work)

Preferred contribution

- SNF Leaching experiments under aerated conditions
- Pure cladding leaching exp. with ^{14}C analyses

- Advanced thermodynamic calculations
- Molecular modelling of Se in SNF

Nagra's interests in a potential project.

- Cr-doped fuel is already in use in Swiss reactors. Information is needed on:
  - IRF
  - Thermodynamics and oxygen potential
  - Dissolution rate

- Behavior of MOX fuel (limited available data)

- High burnup/FGR fuel: is dissolution suppressed in reducing conditions in the same way as it does with low FGR fuel?


THANK YOU !