Karlsruhe Institute of Technology

UNIVERSITÉ DE STRASBOURG

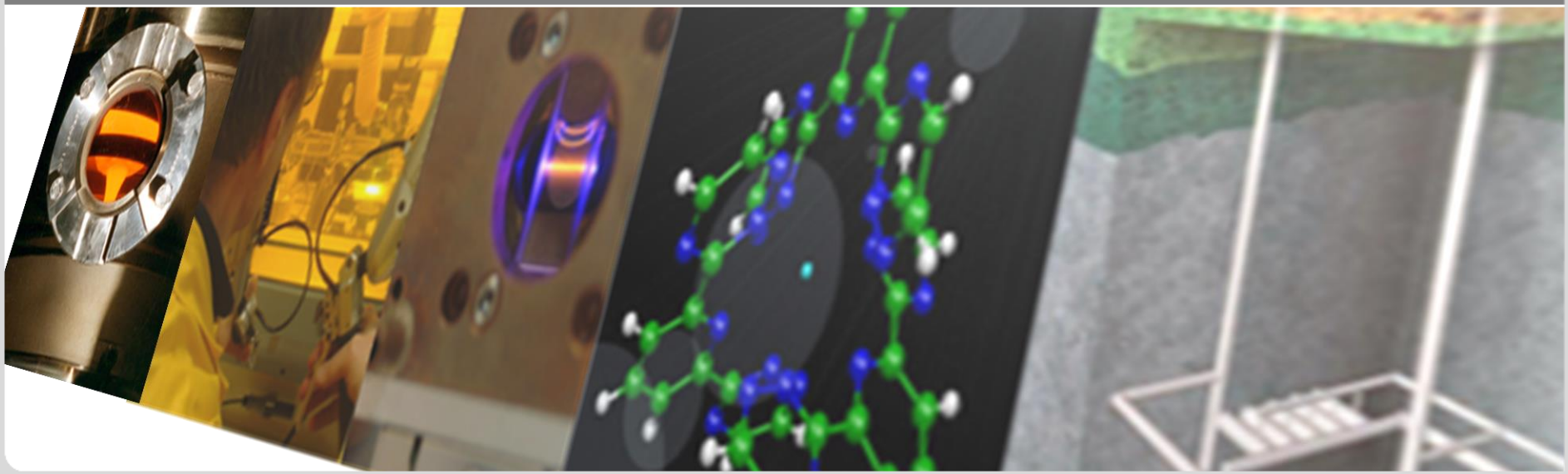
Research at the Institute for Nuclear Waste Disposal (INE)

European Summerschool:

Radiation Measurements and Radiochemistry in Environment and Decommissioning

01.-05.07.2024

INSTITUT FÜR NUKLEARE ENTSORGUNG (INE)



Karlsruhe Institute of Technology

European Summer School

Radiation Measurements and Radiochemistry in Environment and Decommissioning

Visit at the Institute for Nuclear Waste Disposal (INE), Karlsruhe Institute of Technology (KIT)

03 July 2024

Programme

07:15 h	**Bus to KIT**	
09:00 h	**Arrival at KIT-Campus North entrance**	
09:30 h	**Welcome at INE and Introduction**	*H. Geckeis*
09:45 h	**Research towards radioactive waste disposal at KIT-INE**	*H. Geckeis*
10:30 h	**Accelerator Mass spectrometry (AMS) for radionuclide analysis**	*F. Quinto*
11:15 h	**Decommissioning of nuclear facilities**	*C. Krauss*
12.00 h	**Transfer INE - Casino**	
12:15 h	**Lunch**	

Karlsruhe Institute of Technology

13:45 h	**Transfer Casino - KARA**	
14:00 h	**Visit: Synchrotron based X-ray spectroscopic characterization of radionuclides**	*J. Rothe*
17:00 h	**End of visit**	

Topics

- What is KIT?
- Nuclear waste disposal in Germany
- Research at the Institute for Nuclear Waste Disposal

Karlsruhe Institute of Technology

KIT – The Research University in the Helmholtz Association

Status: March 2024

Figures and Facts 2023

48 Spinoffs and startups

5 Campuses – **200** ha area

414 Professors and executive scientists

358 Trainees

22,816 Students

300 Buildings with a usable area of **493,000 m²**

3,244 Doctoral students

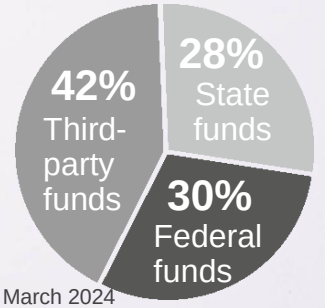
38 Patent applications

10,034 Employees

1,686 International scientists

KIT budget 2023

EUR 1163,1 million



Status: March 2024

KIT – Research and Innovation at 6 Locations

Campus North

Campus South

Campus East

Campus West

Campus Alpine

Helmholtz Institute Ulm

KIT Research Profiles

Five Discipline-focused **Divisions**

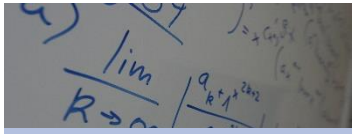
Division I	Division II	Division III	Division IV	Division V
Biology, Chemistry, and Process Engineering	Informatics, Economics, and Society	Mechanical Engineering and Electrical Engineering	Natural and Built Environment	Physics und Mathematics

Nine Interdisciplinary **KIT Centers**

Energy

Mobility Systems

Materials



Mathematics

Health Technologies

Humans and Technology

Climate and Environment

Elementary Particle and Astroparticle Physics

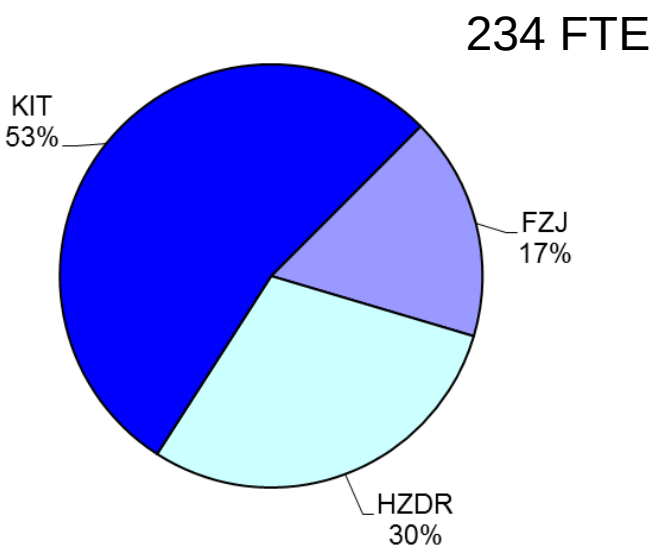
Information · Systems · Technology

The research programme NUSAFE

Nuclear Waste Management and Safety as well as Radiation Research

HELMHOLTZ ASSOCIATION

NUSAFE resources:



67% Nuclear Waste Management

33% Reactor Safety

Topics

- What is KIT?
- Nuclear waste disposal in Germany
- Research at the Institute for Nuclear Waste Disposal

German policy: „Nuclear Phase-out“

RHEIN-NECKAR-ZEITUNG

15.04.2023

Atomausstieg Neckarwestheim 2

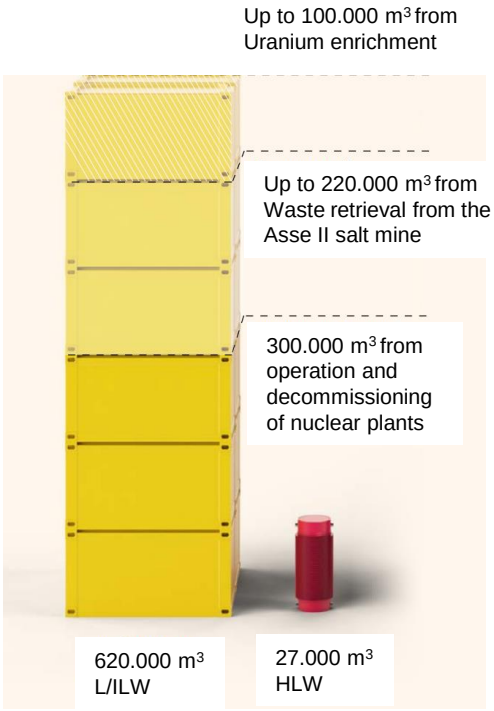
Letztes Atomkraftwerk im Südwesten ist vom Netz gegangen

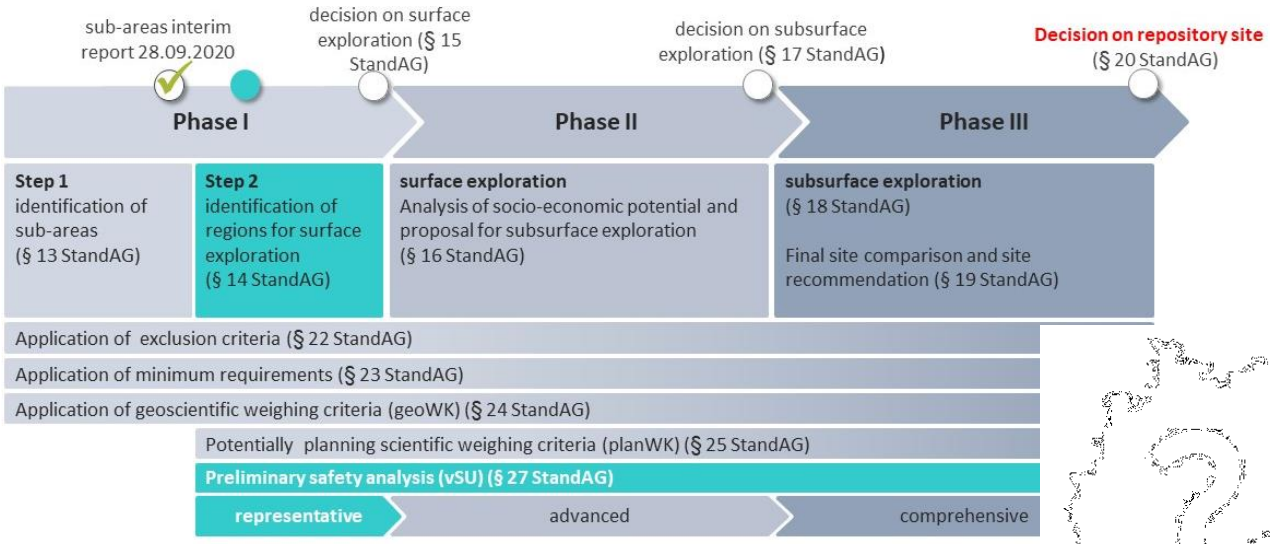
Aus Baden-Württemberg fließt kein Atomstrom mehr ins deutsche Netz. Mit zwei anderen Meilern schreibt das Kernkraftwerk Neckarwestheim 2 Geschichte.

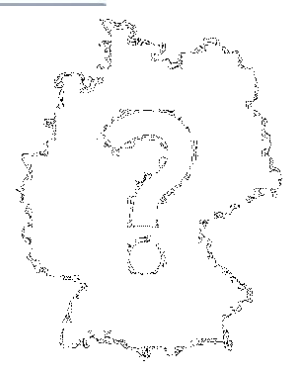
Aus dem Kühlturm am Kernkraftwerk Neckarwestheim steigt Wasserdampf. Mit der Trennung der Kernkraftwerke Isar 2, Neckarwestheim und Emsland vom Stromnetz endete am Samstag die Ära der kommerziellen Stromerzeugung mit Atomkraftwerken in Deutschland. Foto: dpa

Implementation of the German Site Selection Procedure

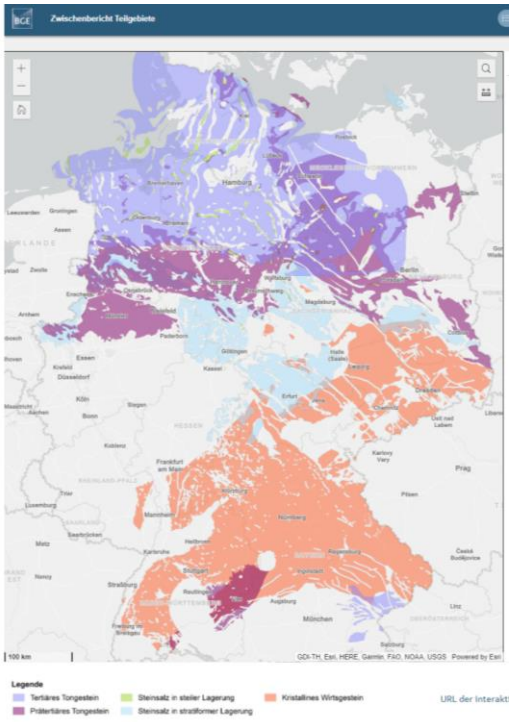
27.000 m³ highly radioactive waste (spent nuclear fuel, vitrified waste)
Up to 620.000 m³ low and intermediate level waste (L/ILW) ➔ licensed repository Konrad mine
+ another L/ILW repository to be decided





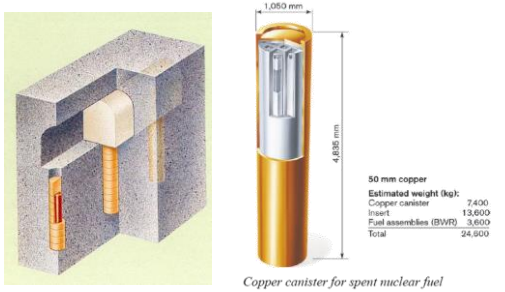


The site selection process (acc. to the German site selection bill, StandAG, 2017)

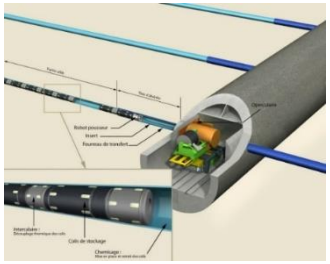


- 54% of the area in Germany is considered worth to be explored

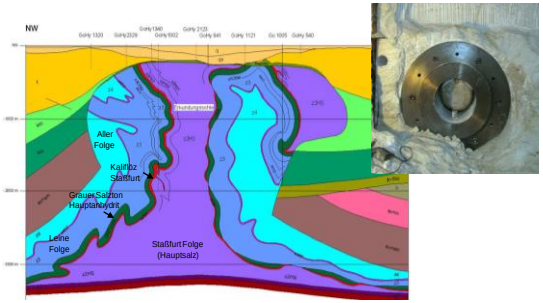
- 90 site areas
  (60 salt domes, 14 stratiforme rock salt layers, 9 clay rock, 7 crystalline rock areas)



Crystalline rock



Argillaceous rock



Rock salt

Topics

- What is KIT?
- Nuclear waste disposal in Germany
- Research at the Institute for Nuclear Waste Disposal

Institute for Nuclear Waste Disposal (INE) @ KIT

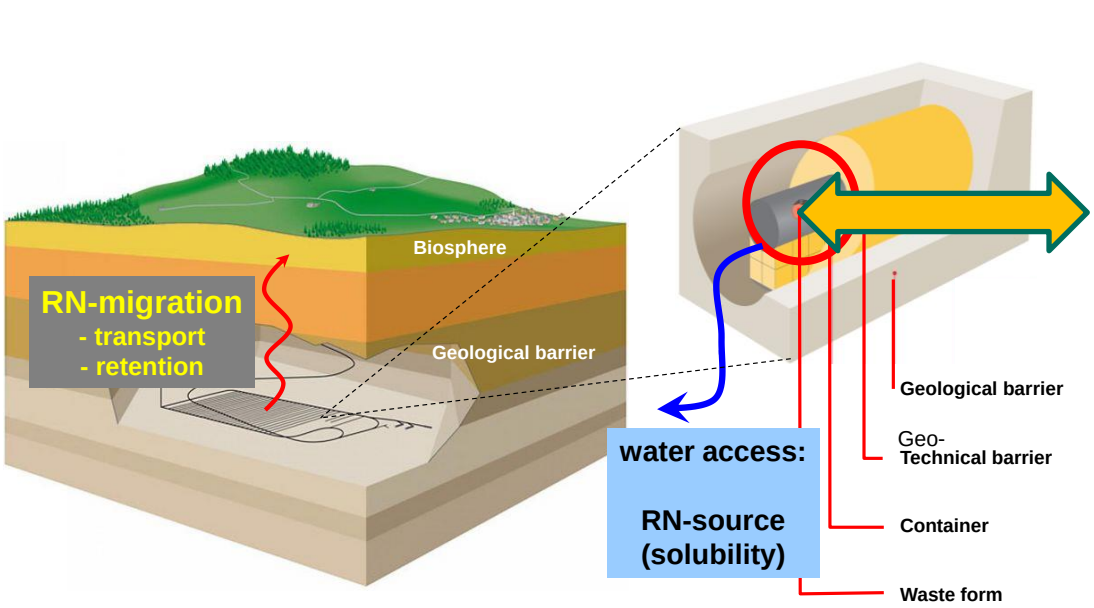
Research and development activities at KIT-INE are an integral component of national provident research and encompass the following areas:

- **Long-term safety research for nuclear waste disposal**
- **Predisposal** – *decommissioning, extended interim storage*
- **Fundamental actinide chemistry**
- **Geothermal energy**

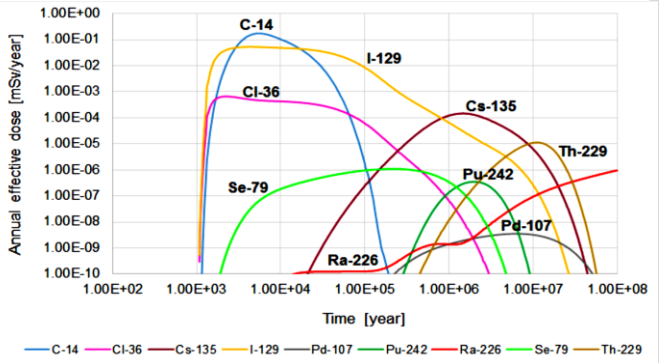
Nuclear waste disposal research at KIT-INE

How do radionuclides and radioactive waste behave in a deep geological repository?

- Safety concept of repositories for nuclear waste disposal relies on the multibarrier system → prevent / minimize the release of radionuclides into the biosphere.



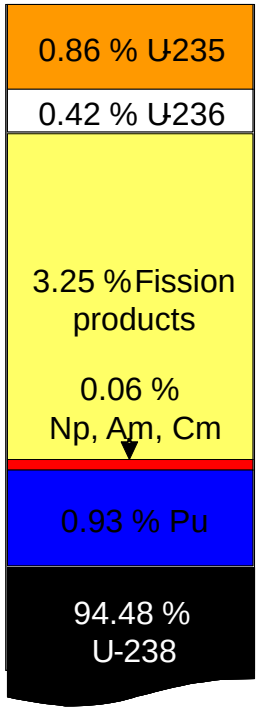
Nagra (2014)



[FLA18]: D. Flamikova, V. Necas, *Creation of Reference Biosphere Model for Safety Assessment of Deep Geological Repository*, AIP Conference Proceedings 1996, 020009 (2018).

Content of high-level nuclear waste

spent fuel



PWR; Burn-up 33GWd/tU

Some long-lived fission and activation products

C-14	($t_{1/2}$ ~ 5.700 a)
Cl-36	($t_{1/2}$ ~ 300.000 a)
Se-79	($t_{1/2}$ ~ 360.000 a)
Tc-99	($t_{1/2}$ ~ 213.000 a)
I-129	($t_{1/2}$ ~ 15,6 Ma)

Important Transuranium elements:

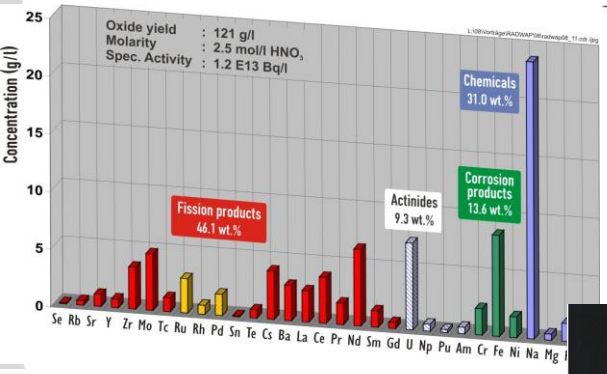
Pu-238 ($t_{1/2}$ ~ 88 a)

Pu-239 ($t_{1/2}$ ~ 24.110 a)

Am-241($t_{1/2}$ ~ 432 a)

Cm-243($t_{1/2}$ ~ 29 a)

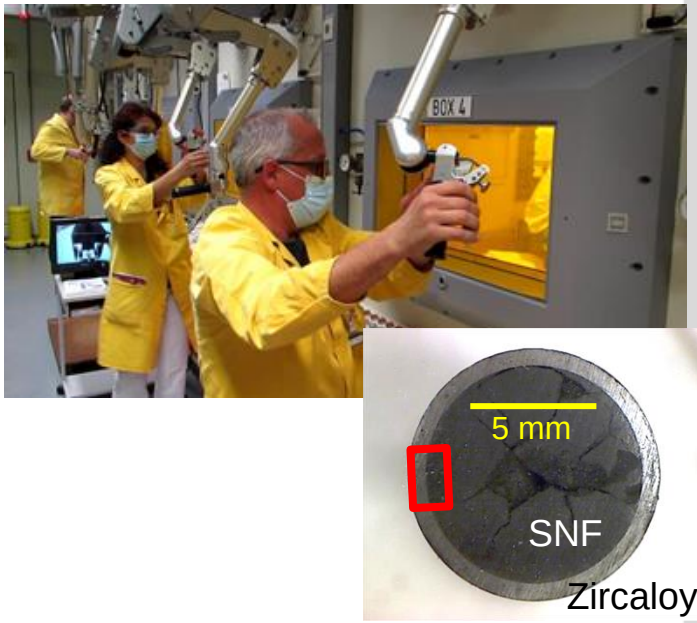
Np-237 ($t_{1/2}$ ~ 2.1 Ma)



Vitrified liquid waste

Project examples

Research on spent nuclear fuel (SNF) assemblies

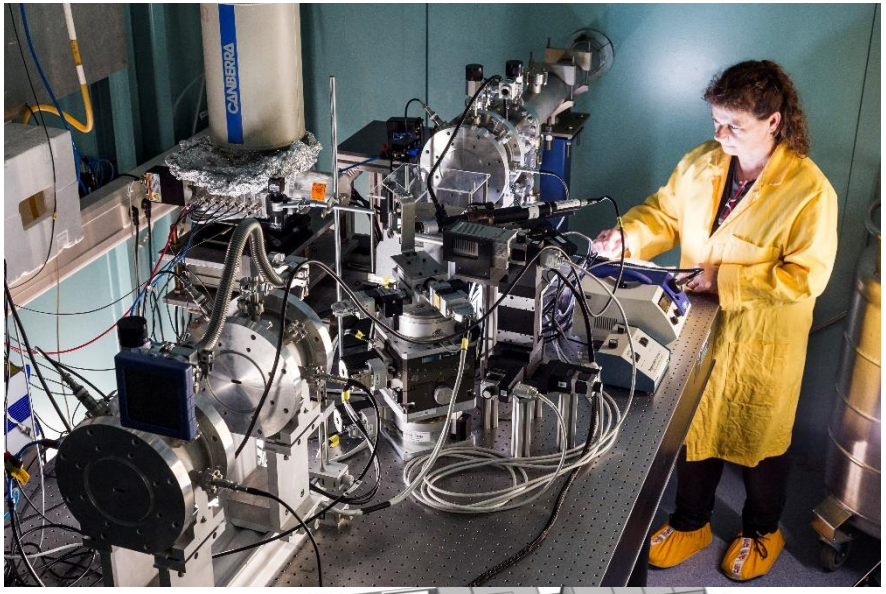


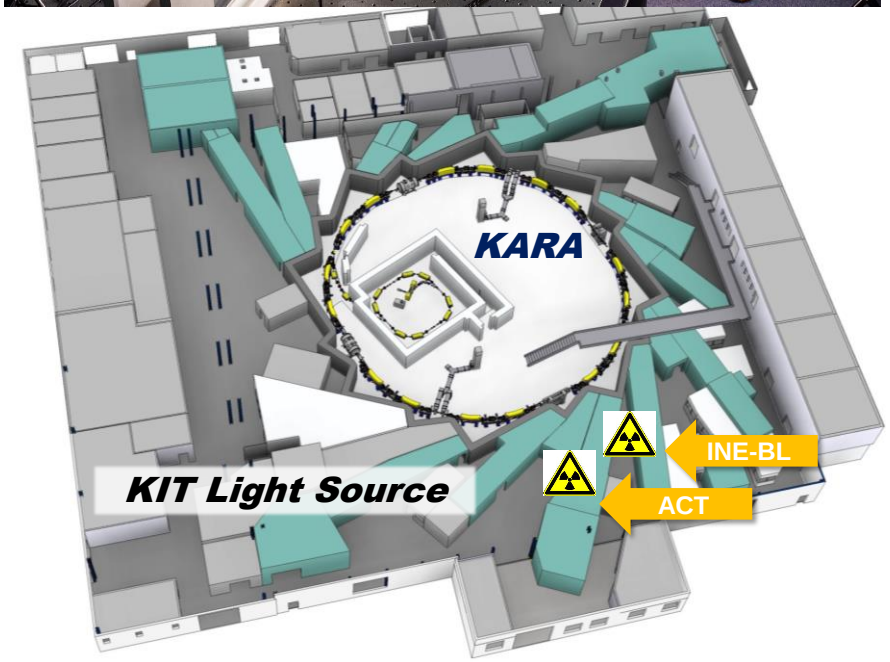
- **Quantification of ^{129}I and ^{36}Cl inventories in irradiated SNF and zircaloy:**
  - **for the 1st time radio-chemical analysis of ^{36}Cl in irradiated Zircaloy, MOX and UO_2 fuels** → good agreement between analyses and MCNP calculations for ^{36}Cl in claddings.

PhD thesis: T. König

Project examples

Analysis by X-Ray Vision

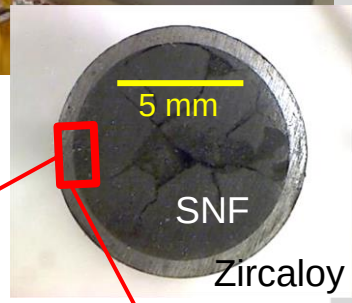


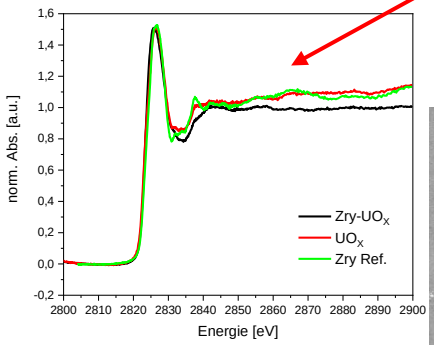


Project examples

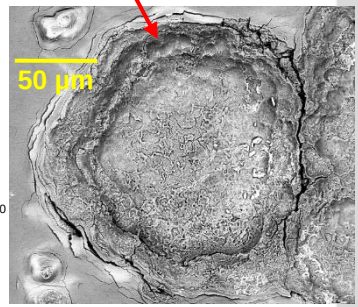
Research on spent nuclear fuel (SNF) assemblies

- **Quantification of ^{129}I and ^{36}Cl inventories in irradiated SNF and zircaloy:**
  - **for the 1st time radio-chemical analysis of ^{36}Cl in irradiated Zircaloy, MOX and UO_2 fuels** → good agreement between analyses and MCNP calculations for ^{36}Cl in claddings.
  - $^{36}Cl^-/^{129}I^-$ exists in mixed solid phases (Cs, Te, Ba, U, Pu)
  - Cl K-edge XANES characterization points to chemical environment different to CsCl





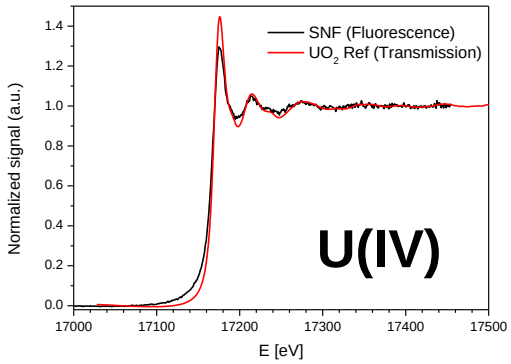
Chlorine K-XANES

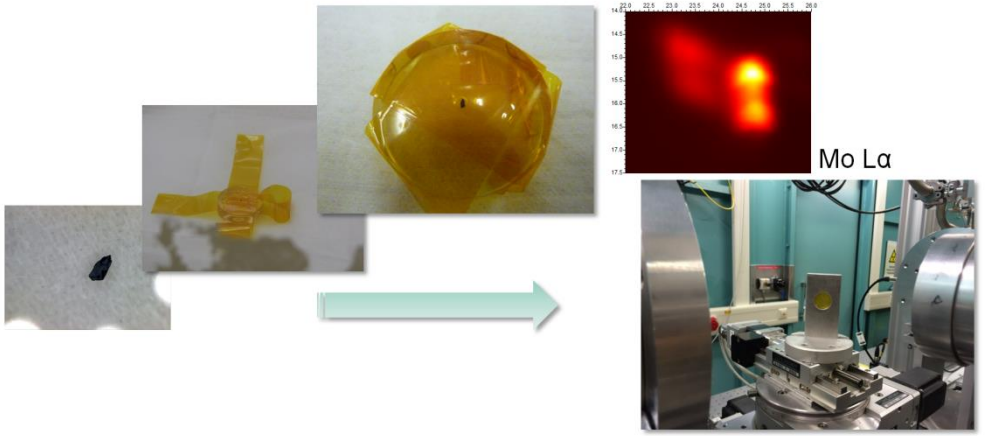


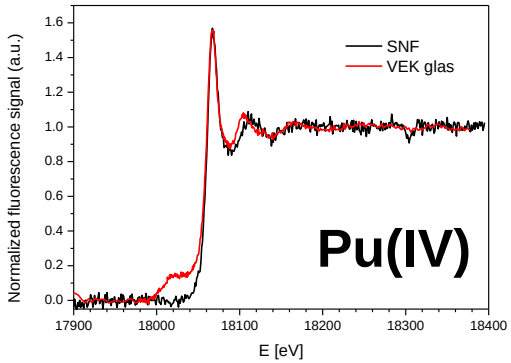
- **Pellet-cladding interactions (simulated)**
  - Indications for **formation of complex Cs-U-O-Zr-Cl-I compounds** and consecutive **pitting corrosion in cladding** observed at <400°C (interim dry storage conditions)

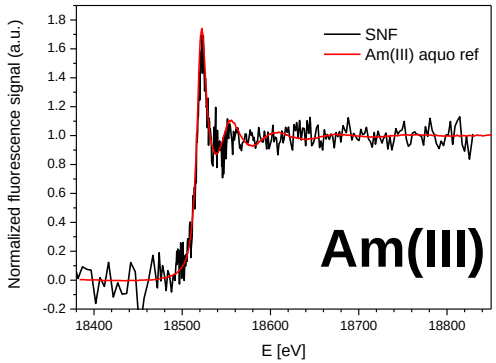
PhD thesis: T. König

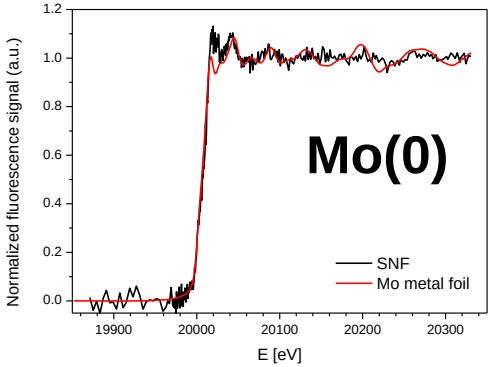
XAFS/XRF investigation of a SNF particle sampled from a test fuel rod irrad. at the Gösgen (CH) PWR









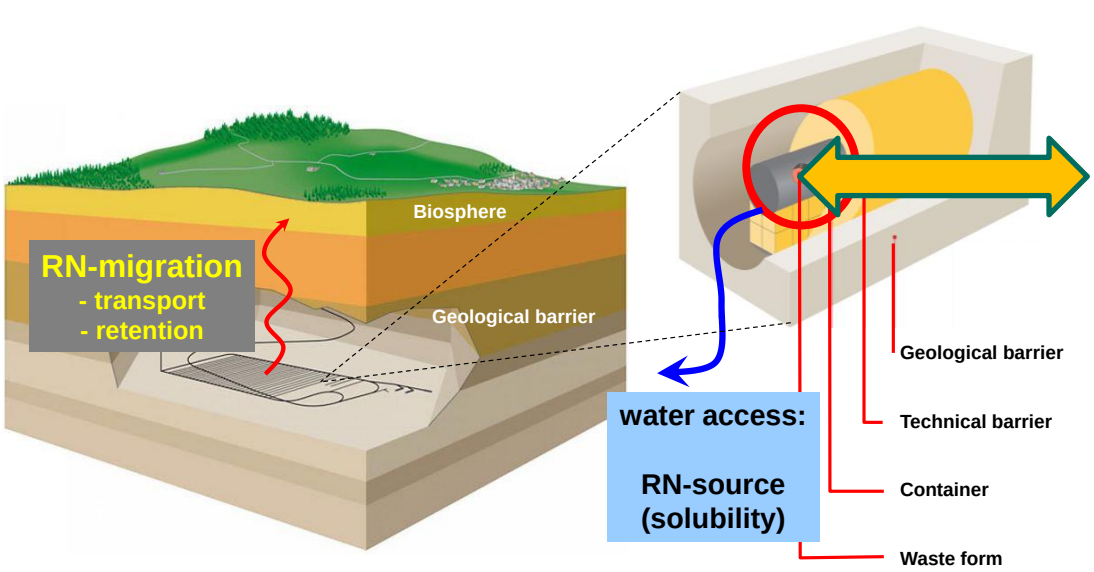


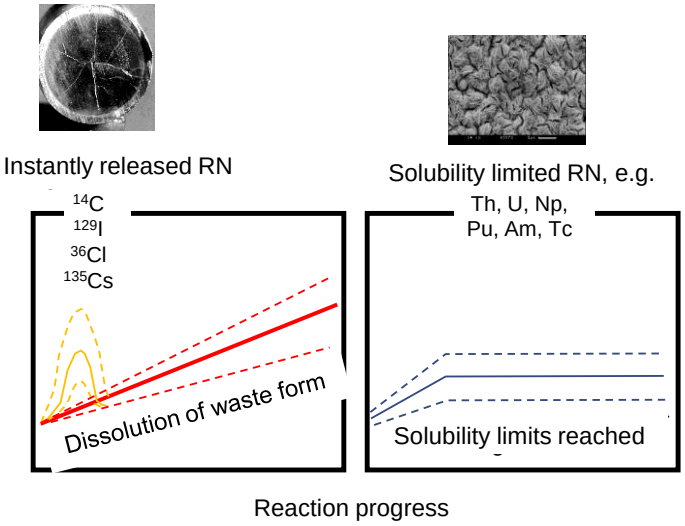
XAFS:

- Zr and Mo are found as Zr(IV) and Mo(0) (metallic state) in the SNF particle – the actinides in the oxidation states U(IV), Pu(IV), Am(III)

Nuclear waste disposal research

- Safety concept of repositories for nuclear waste disposal relies on the multibarrier system → prevent / minimize the release of radionuclides into the biosphere.





Nagra (2014)

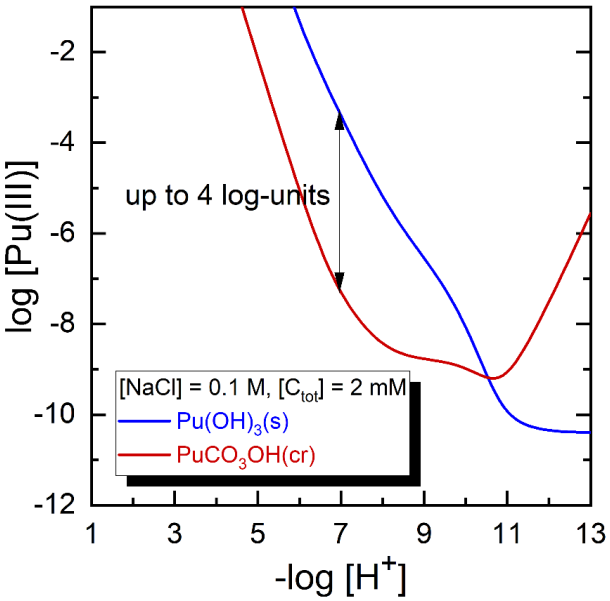
Project examples

The role of $PuCO_3OH(cr)$ to limit Pu-solubility

- Reduction of PuO_2^{2+} to Pu^{3+} (electrolysis), and precipitation as $Pu(OH)_3(s)$
- Equilibration of $Pu(OH)_3(s)$ in Na-HCO_3-CO_3 solution at pH ≈ 8
- After 10 months: transformation of $Pu(OH)_3(s)$ into a ***blue fine crystalline solid***

PhD thesis: P. Müller

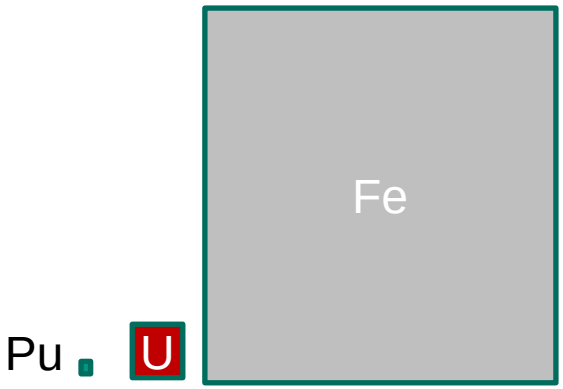
* **"sink" for Pu(III)** at near-neutral pH
* forms **spontaneous** from $Pu(OH)_3(s)$

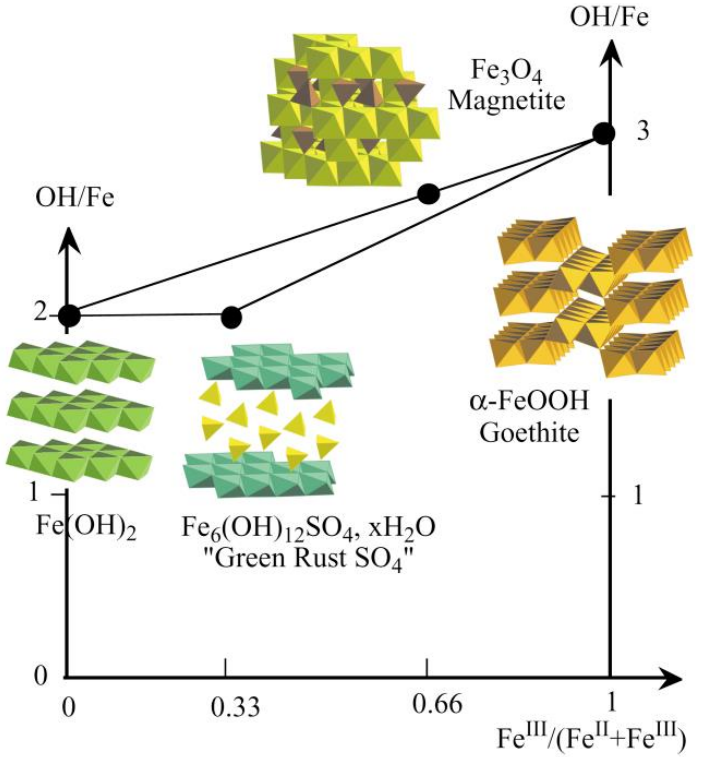


Barrier function of container corrosion products

- Repository for high-level nuclear waste inventory:

  molar ratio Fe:U:Pu ~ 40-50:1:0,01



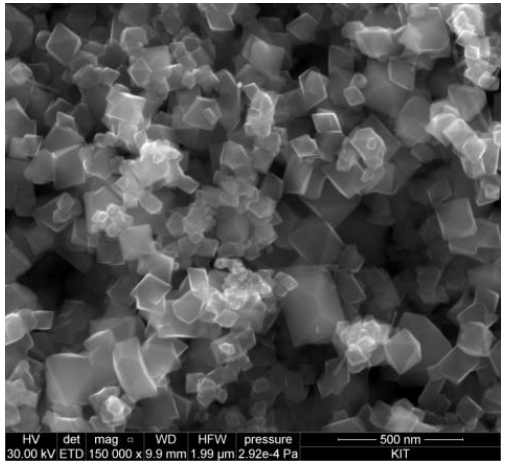


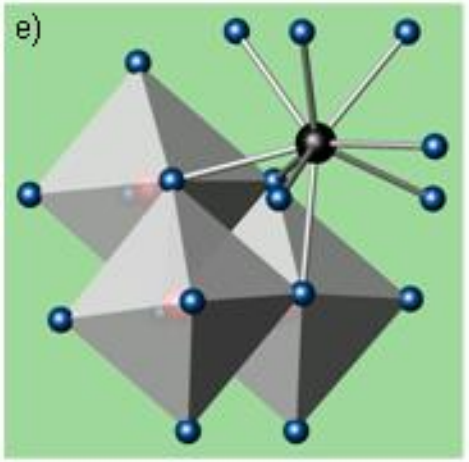
Jolivet *et al.*, Chem. Commun. **2004**, 481-487

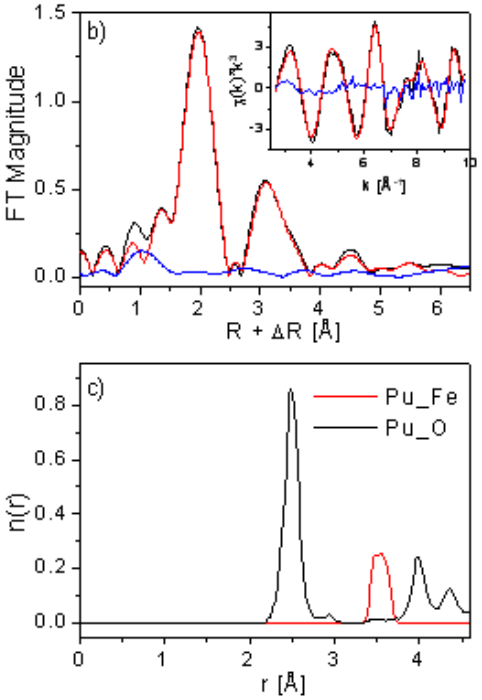
Barrier function of container corrosion products

- Interaction of trivalent actinide ions with magnetite -

Pu interaction with magnetite (Kirsch, Scheinost et al. ES&T, 2011)

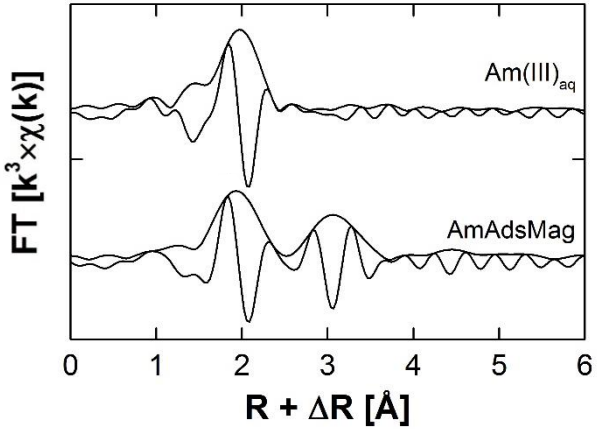






Pu-LIII EXAFS investigation of the Pu+Magnetite system

Am interaction with magnetite (Finck et al., 2015)



Am-O:	2.47 Å
Am-Fe:	3.50 Å

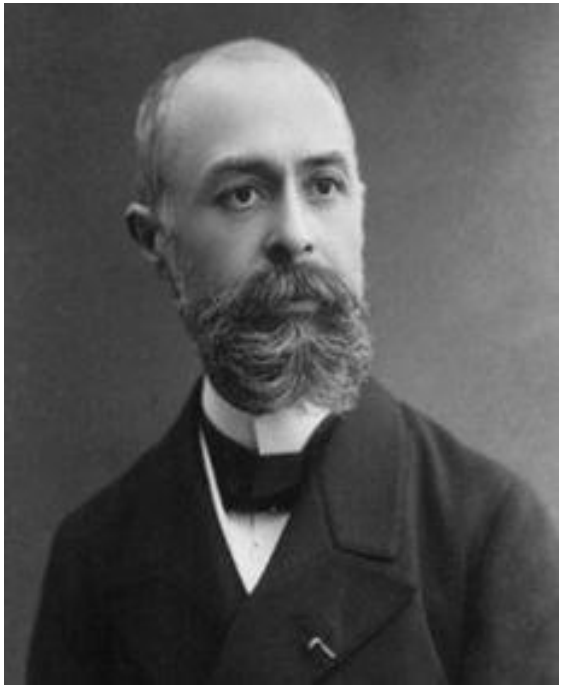
Finck, Nedel, Dideriksen, Schlegel, 2015

Pu(III)-O:	2.48 Å
Pu(III)-Fe:	3.54 Å

Kirsch, Scheinost et al. ES&T, 2011

Laser technology ….
… for analysis ?

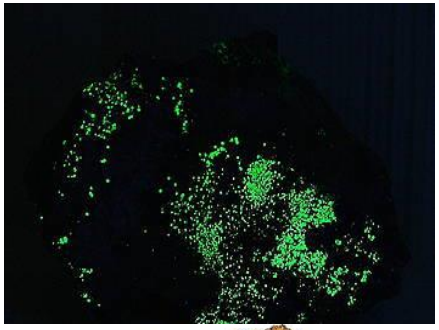
Times are changing …..

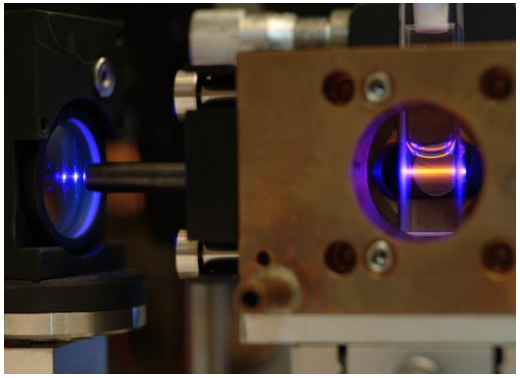


Antoine Henri Becquerel (1852-1908)

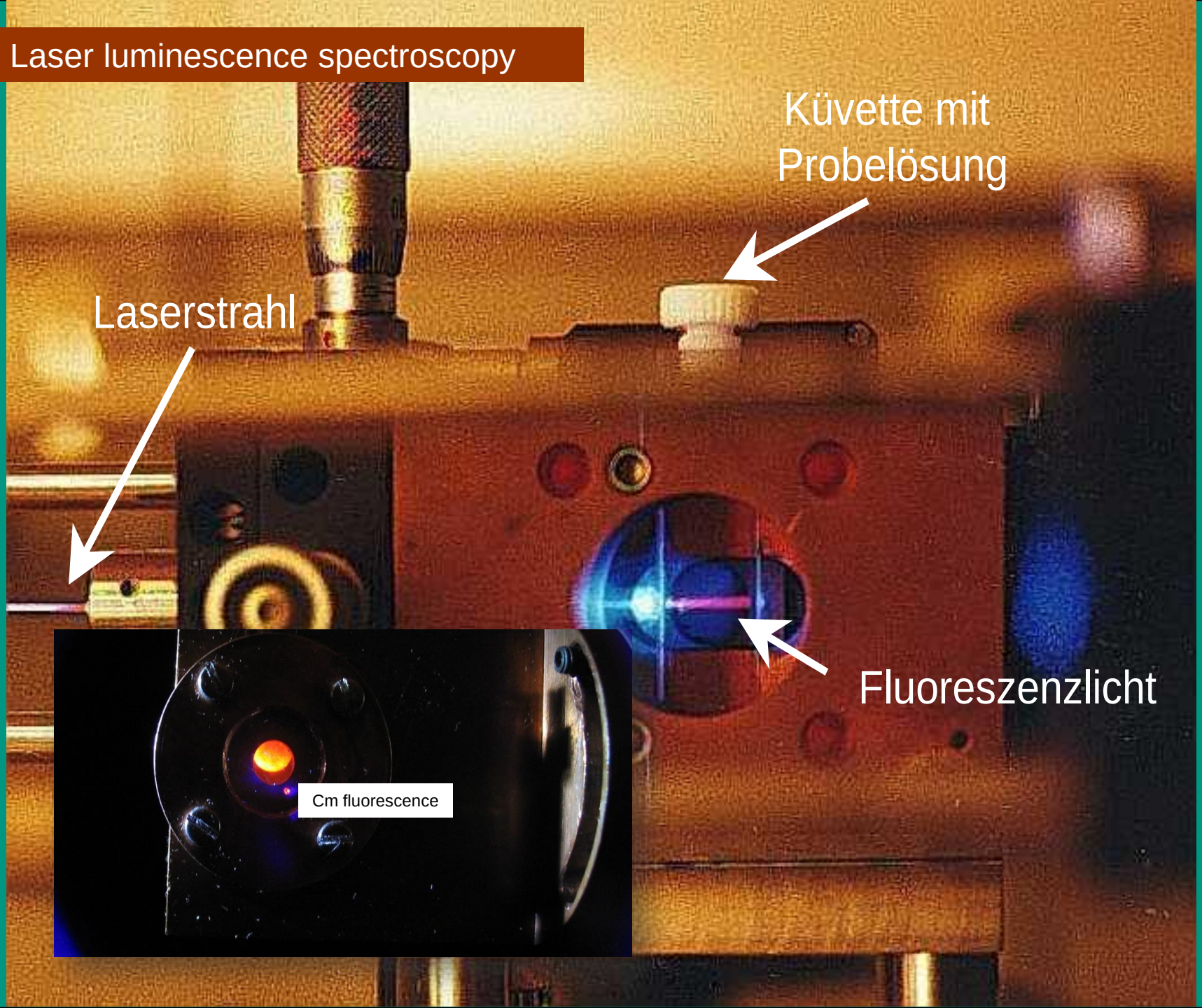
Becquerel studied 1896 the luminescence of
$K_2UO_2(SO_4)_2*2H_2O$
and discovered radioactivity

Today, we study chemistry of radioactive elements by observing their luminescence

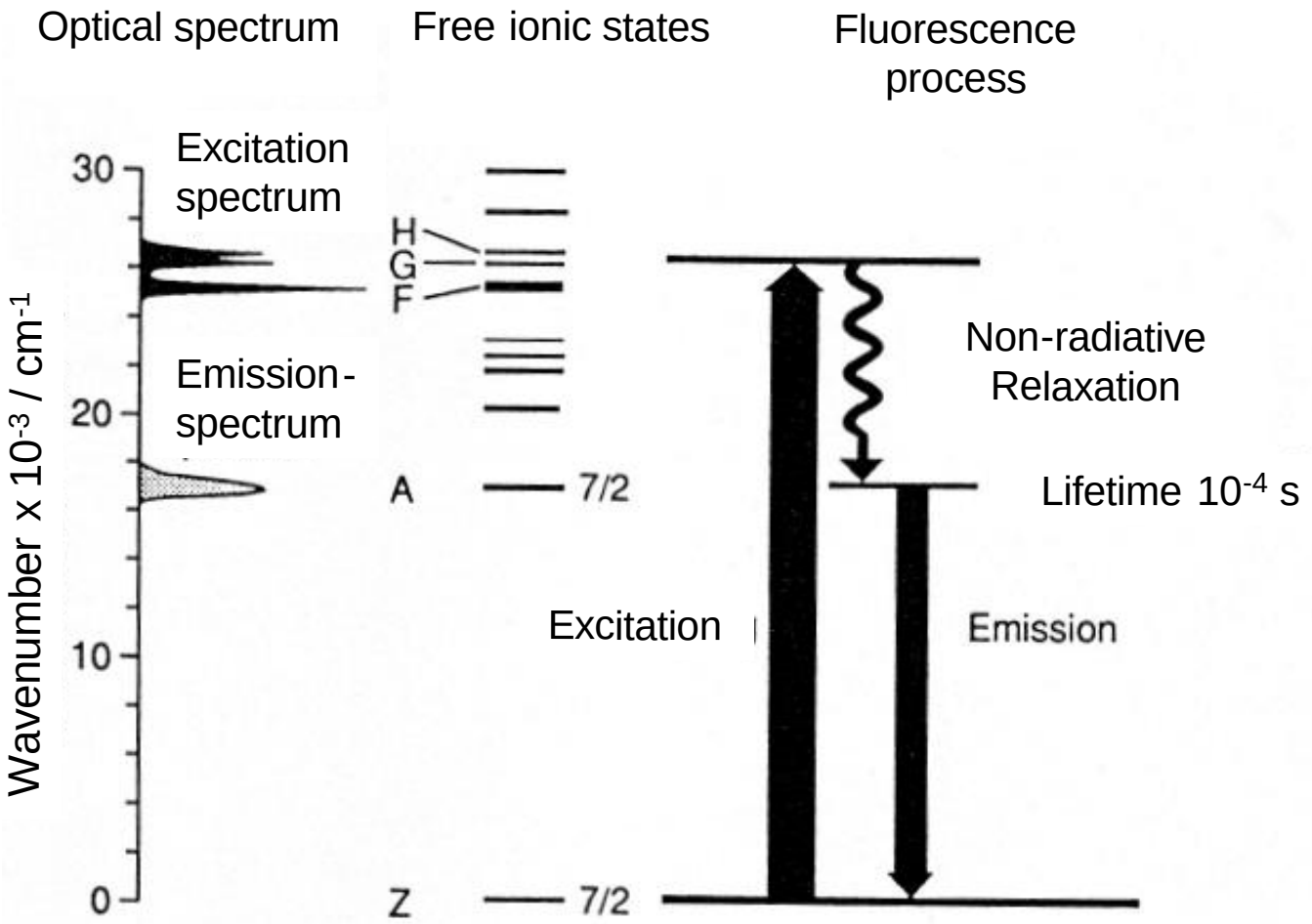




Laser luminescence spectroscopy

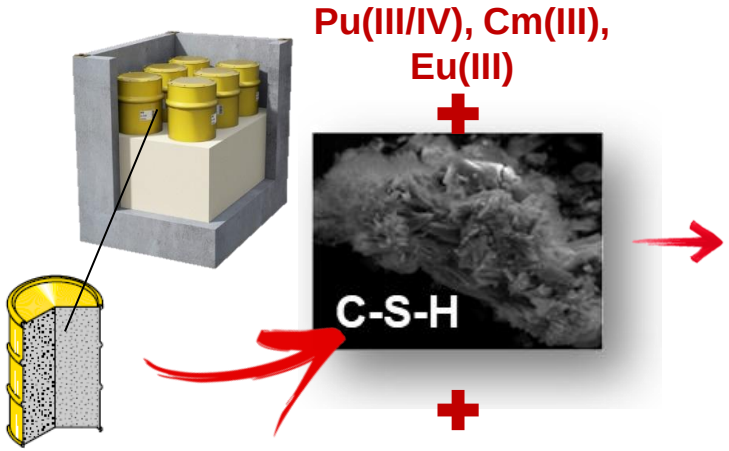


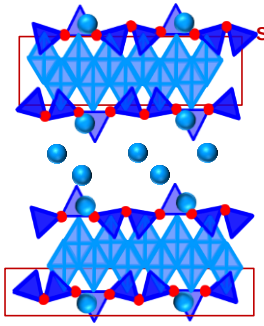
The Time Resolved Laser-Fluorescence Spectroscopy
- The basic principle -

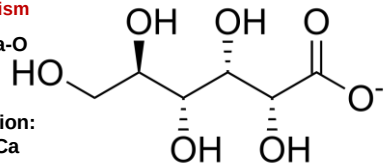


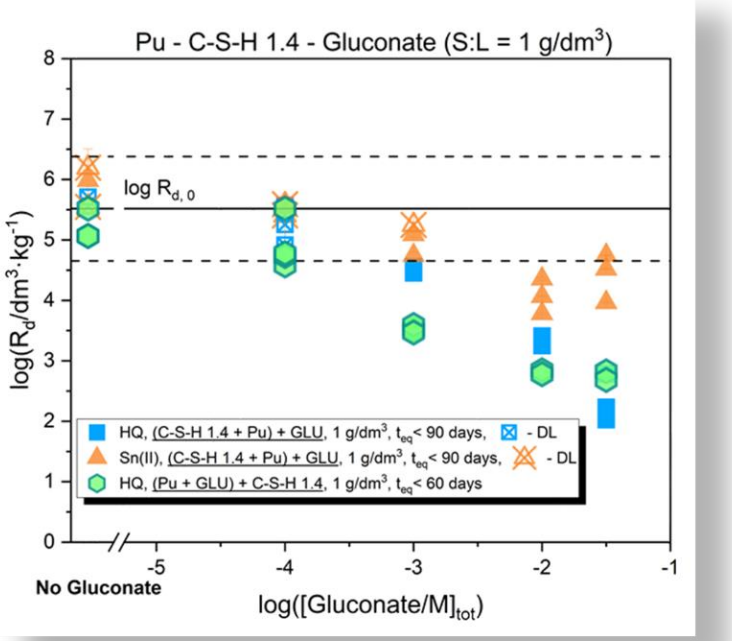
Project example:

Impact of organic cement plasticisers on actinide solubility









Retention behavior

PhD thesis: R. E. Guidone

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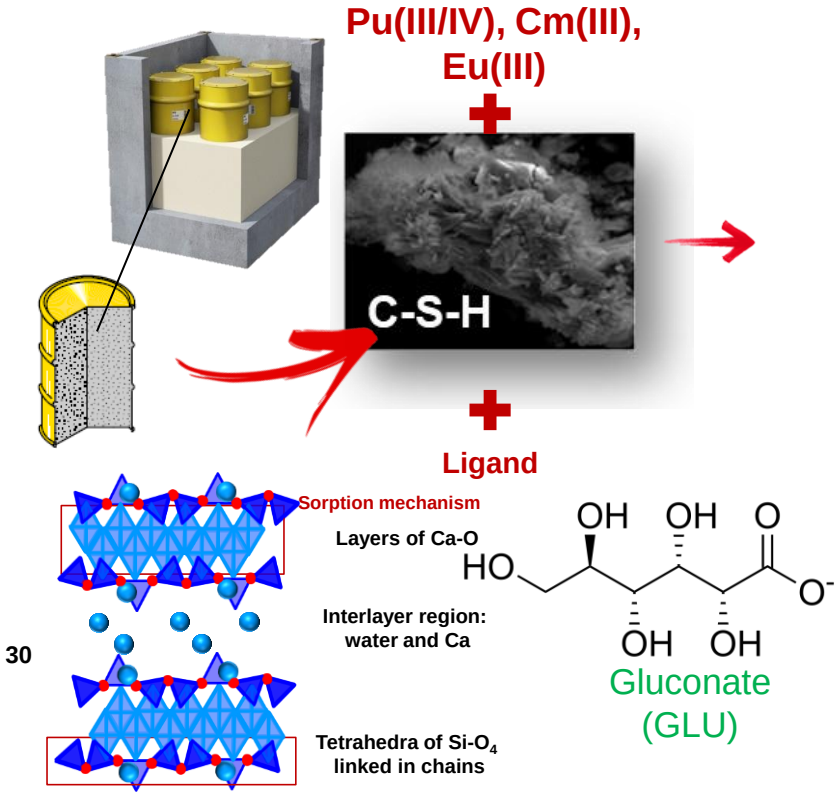
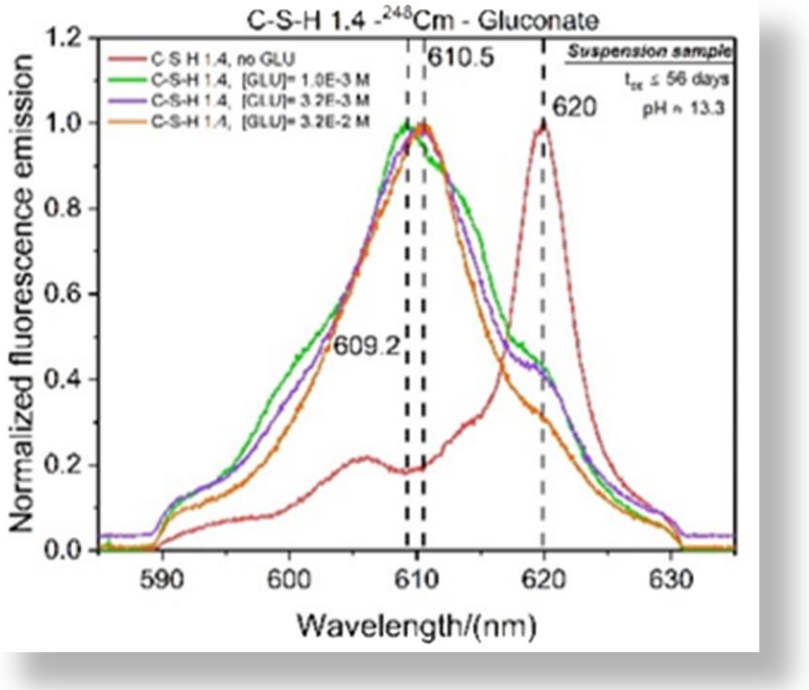
Project example:

Impact of organic cement plasticisers on actinide solubility



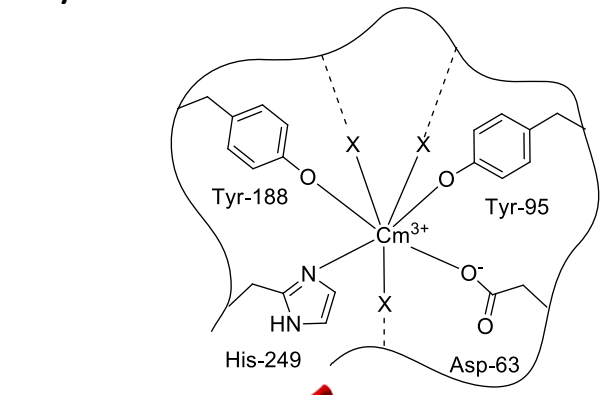
PhD thesis: R. E. Guidone

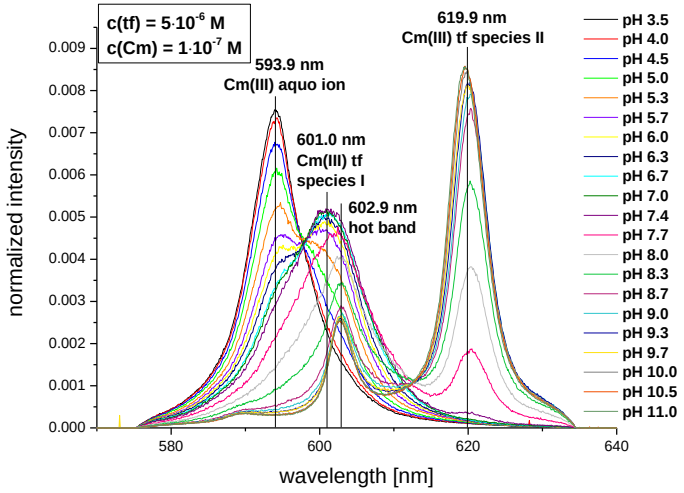


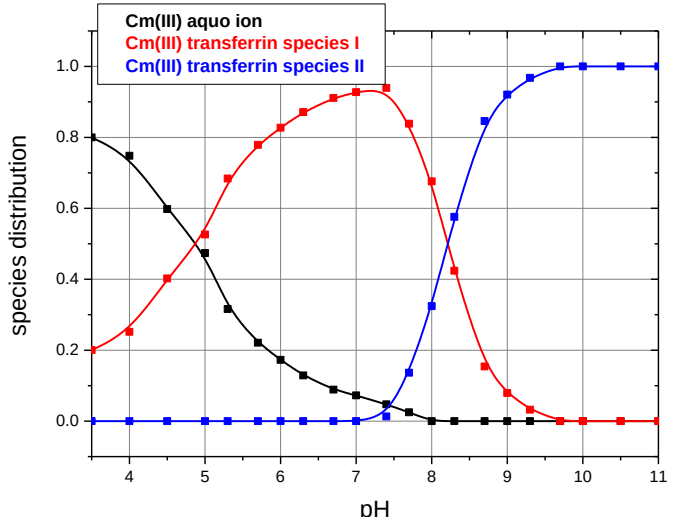
Cm-TRLFS spectra C-S-H suspension

Complexation of transferrin with Cm(III)

A complex with Cm(III) bound at the C-terminal binding site and another metal ion coordinated at the N-Lobe can potentially bind to the receptor and be brought into cells via endocytosis



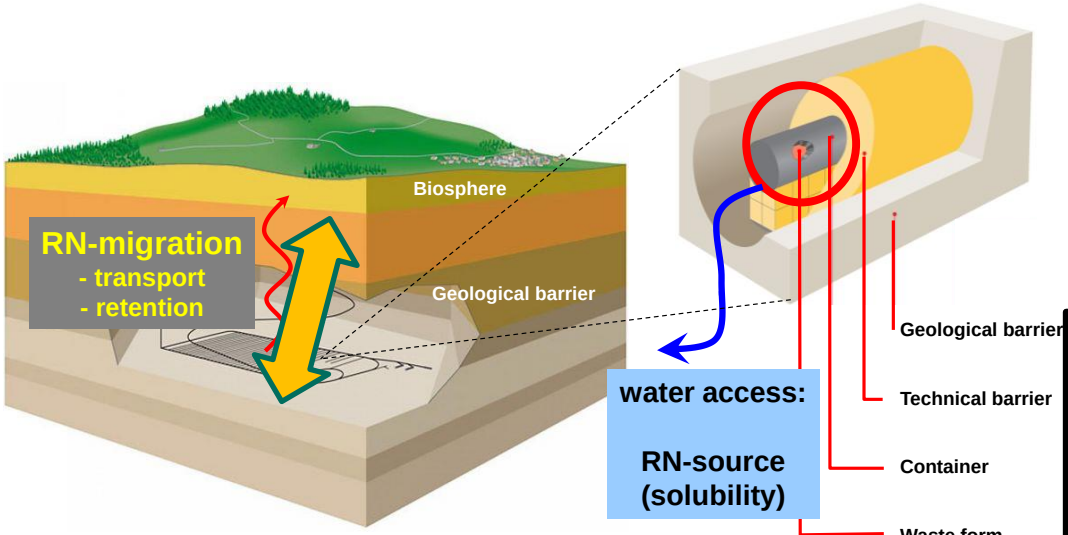




N. Bauer, thesis Uni Heidelberg, 2015

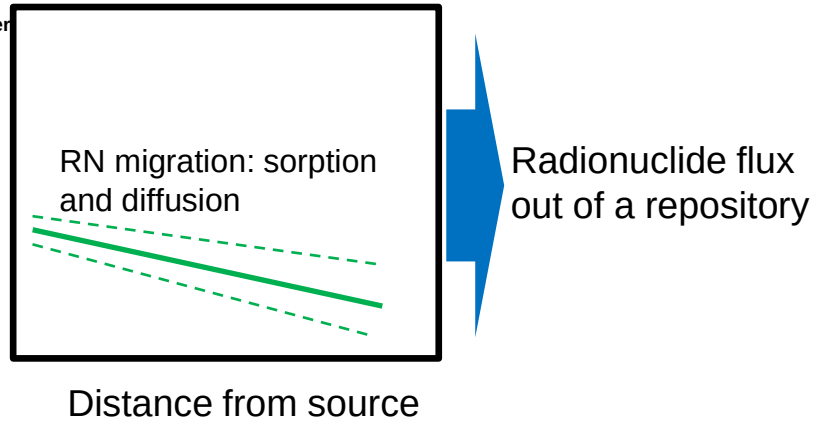
Nuclear waste disposal research

- Safety concept of repositories for nuclear waste disposal relies on the multibarrier system → prevent / minimize the release of radionuclides into the biosphere.

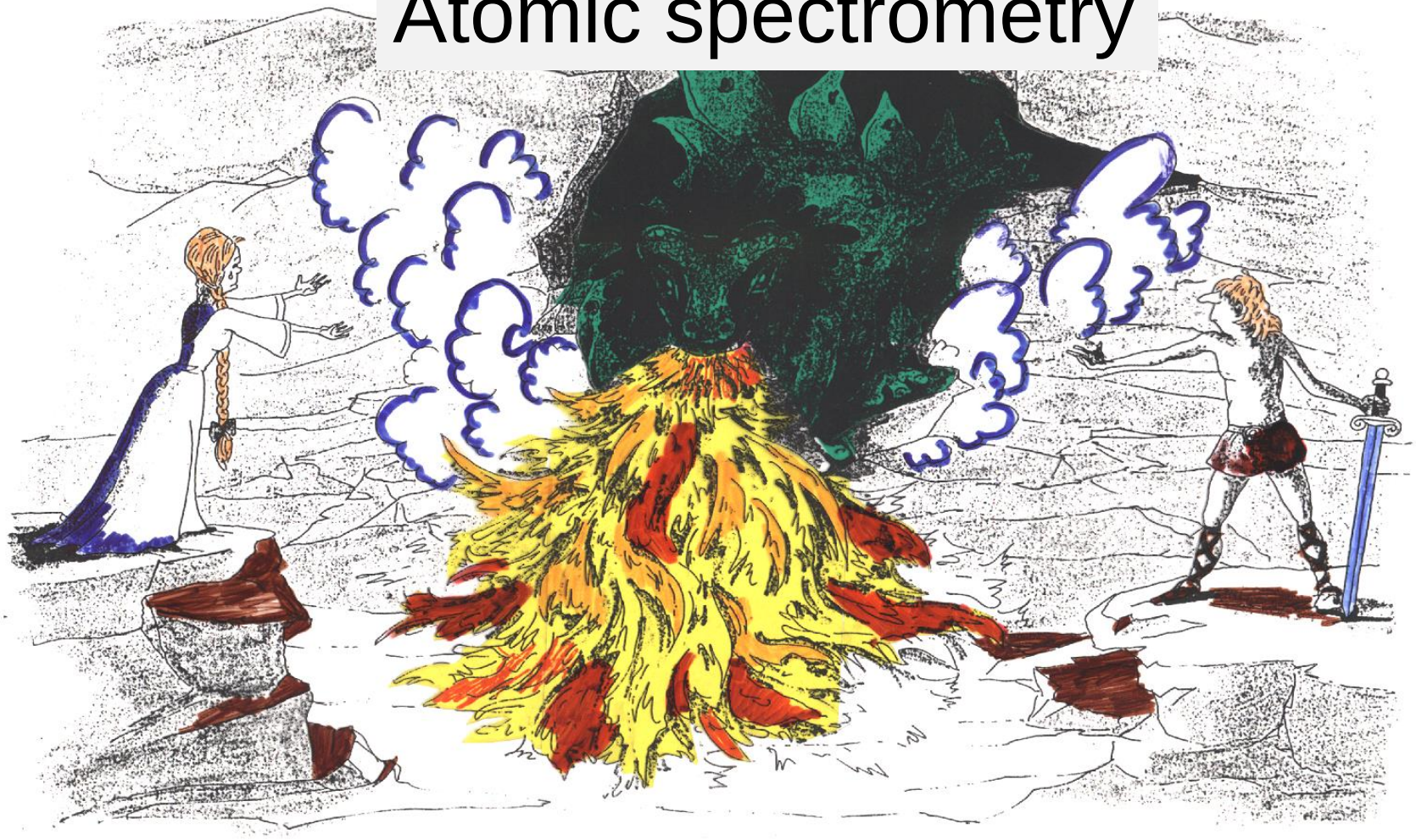


Nagra (2014)

Example: porewater from the Belgian Boom Clay formation

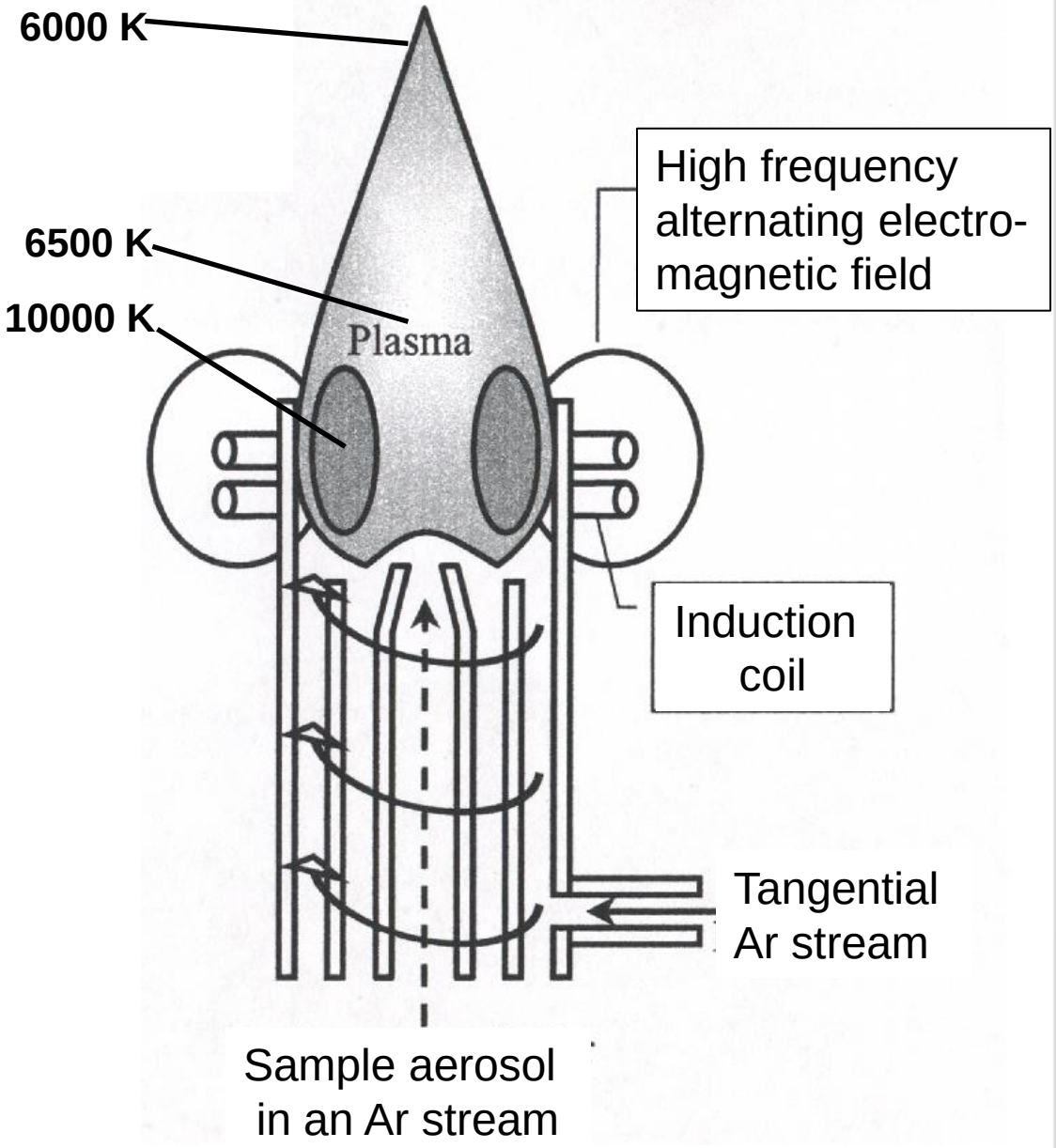


Atomic spectrometry

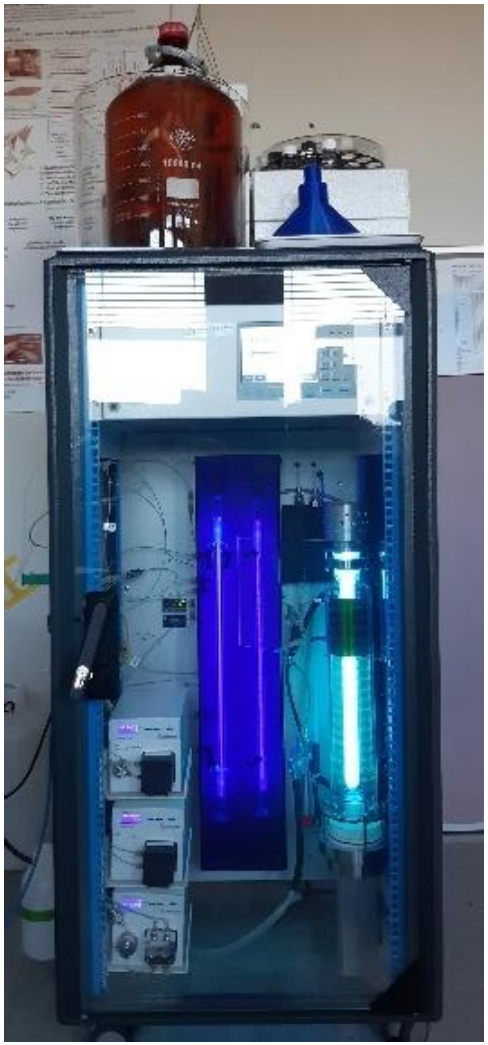


Thermische Dissoziation

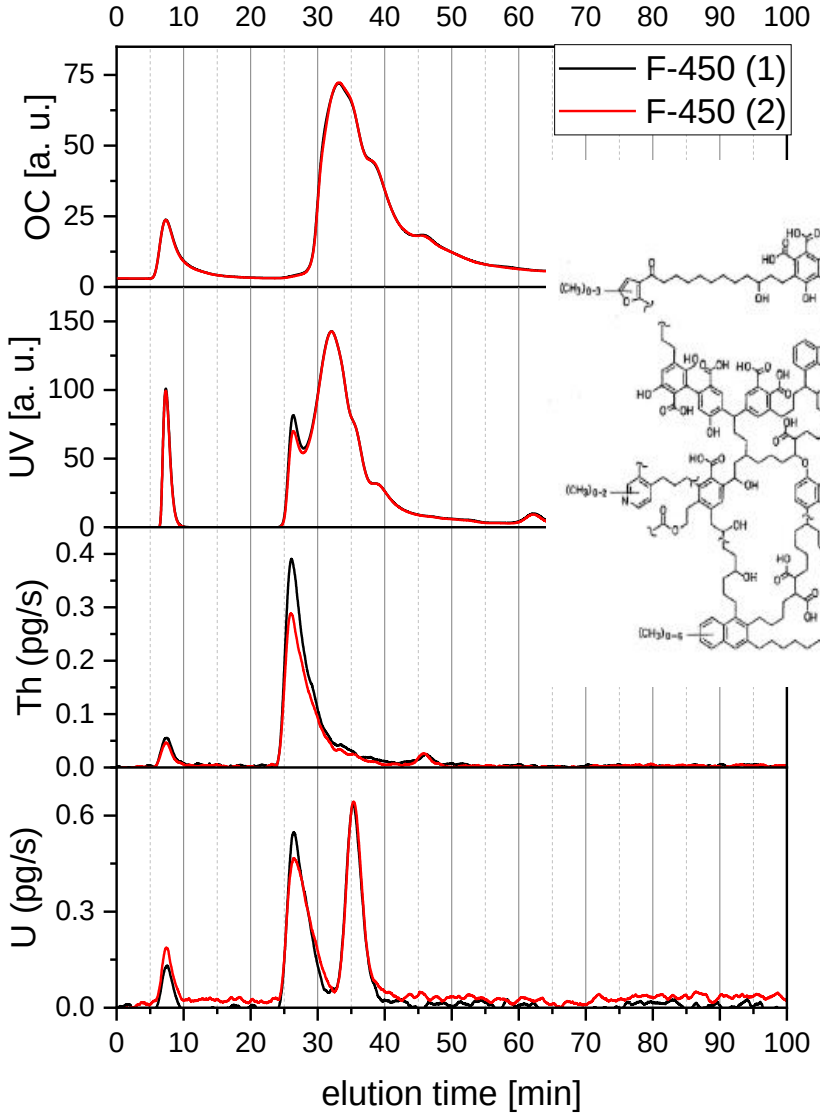
Thermal dissociation

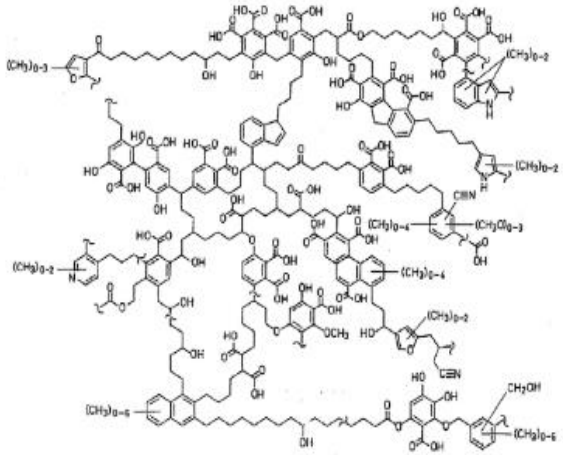

6000 K
6500 K
10000 K
Plasma
High frequency alternating electro-magnetic field
Induction coil
Tangential Ar stream
Sample aerosol in an Ar stream

Colloid-borne naturally abundant U, Th in Boom-Clay porewater



Coupling: LC-OCD-OND-UVD – ICP-MS

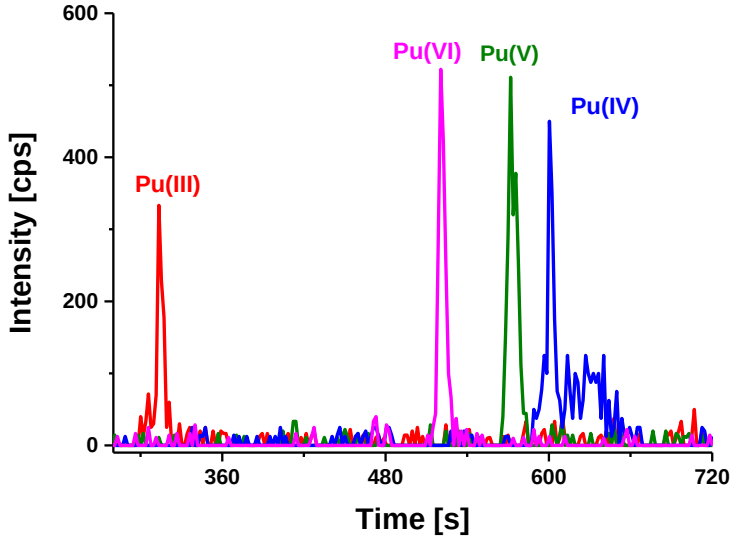




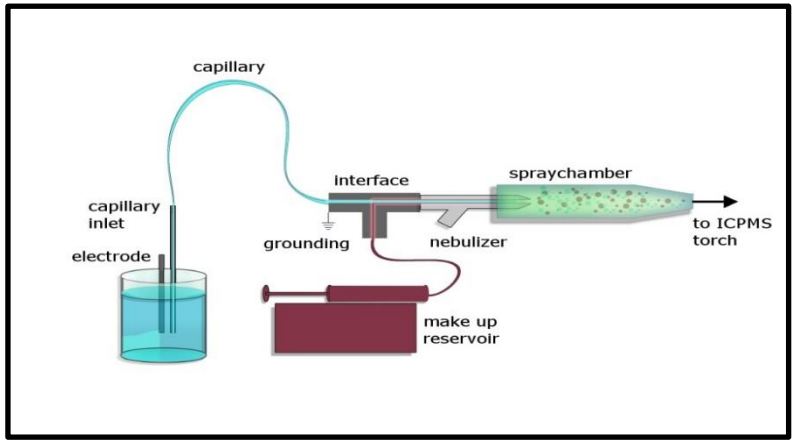
Schulten, Schnitzer, 1997

A. Lunz, Masterthesis, 2022

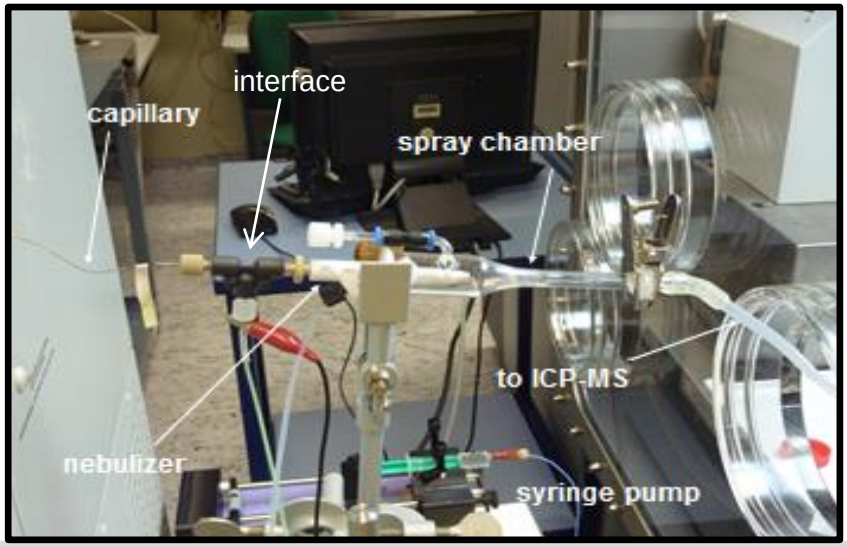
Hyphenation of CE and SF-ICP-MS



Species	Limit of detection [mol·L^{-1}] (3 σ)
^{242}Pu	$2 \cdot 10^{-12}$
^{238}Pu	$5 \cdot 10^{-11}$
^{237}Np	$5 \cdot 10^{-12}$
^{56}Fe	$5 \cdot 10^{-9}$



(Graser, Lagos, Marquardt et al., Anal.Chem., 2015)



KIT - Institute for Nuclear Waste Disposal (INE)