# Radionuclide Retention and Redox

*(WG1, Cement – CEBAMA)*

INSTITUTE FOR NUCLEAR WASTE DISPOSAL

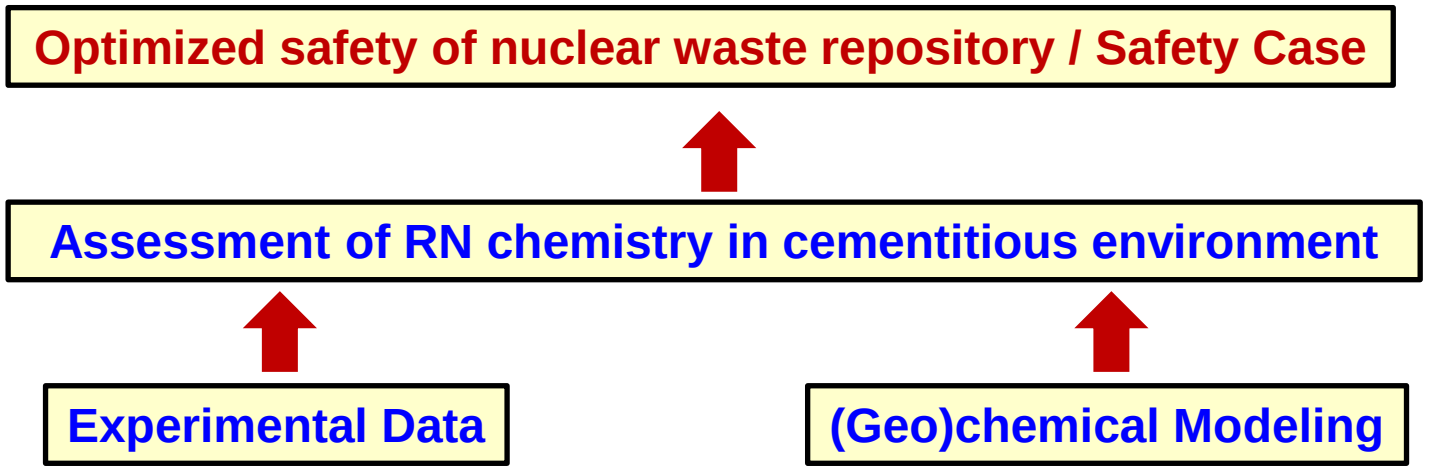
**M. Altmaier, KIT-INE, Germany**

# Introduction

- Specific interactions of radionuclides with cementitious materials can cause either retention or mobilization of long-lived radionuclides.
- Specific research on RN chemistry highly important.
- Advanced understanding and modeling of RN behavior in cementitious systems supports Safety Assessment and helps to develop Safety Case.

# Introduction

- Proposed Collaborative Project (CEBAMA) would enable to
  - *Develop advanced understanding on RN-cement interactions*
  - *Reduce present uncertainties for RN source terms*
  - *Better assess RN retention processes in cementitious environment + presence of organics*
  - *Derive more complete TDB for improved model calculations*
  - *Integrate expertise from advanced and newer projects*
  - *Contribute to knowledge transfer and knowledge maintenance*




- aqueous RN speciation
- solid phases
- redox chemistry
- kinetics
- sorption
- …

- log °$K_{sp}$,
- log °ß,
- solid solutions
- improved sorption models
- …

Need to establish precise experimental data and advanced modeling approaches

# Relevant Radionuclides

- Chemical behavior of both anionic fission products and long-lived actinides need to be understood.

- The calculated risk related to radionuclide mobilization from a repository is dominated by anionic ***fission and activation products***.
  - (Se, I, Cl, C, Tc, …)

- Alpha emitting ***actinides*** are investigated because of their extremely high radiotoxicity and the need to ensure their quantitative retention.
  - (Pu, Am, Np, U, Pa, …)

# Relevant Radionuclide Chemistry

- Chemical mechanism controlling radionuclide (geo)chemistry and retention in cementitious environments include

  *A) Redox reactions involving radionuclides*

  *B) Solubility and dissolution phenomena*

  *C) Sorption and incorporation processes*

- Important aspects for RN chemistry in cementitious systems:
  - *Presence of strongly alkaline solutions*
  - *Strong complexation with organic ligands*

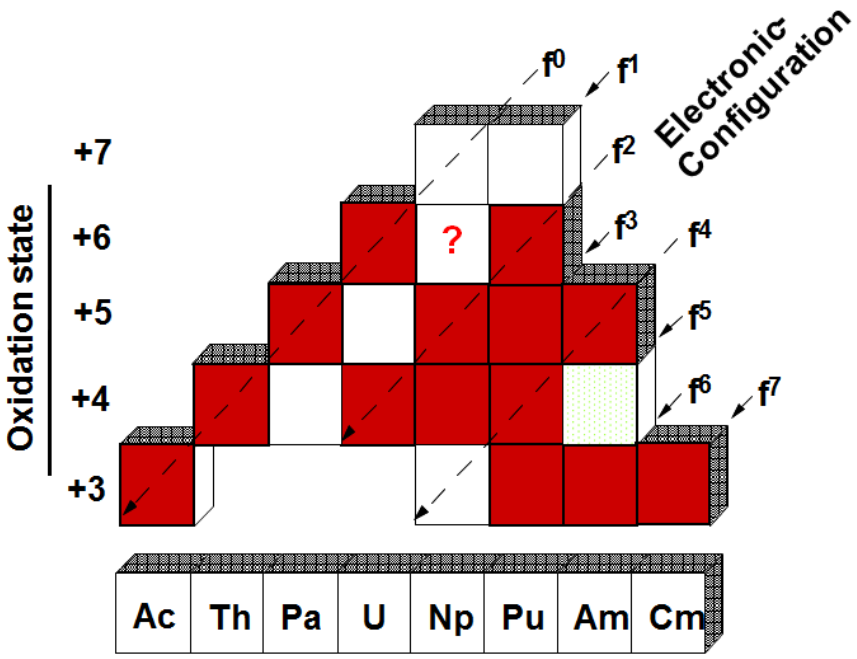
# A) Redox reactions involving radionuclides

- Several important radionuclides exist in more than one oxidation state, each exhibiting distinct chemical properties and differing features.
- Detailed understanding of radionuclide redox chemistry essential.

- RN redox evolves as coupled process:
  - *Factors controlling evolution of redox conditions (Fe from host rock and container, organics from waste and concrete, $H_2$, …)*
  - *RN behavior in response to total redox conditions*

- Redox processes often exhibit slow reaction kinetics – detailed studies required to assess long-term evolution.

# A) Redox reactions involving radionuclides



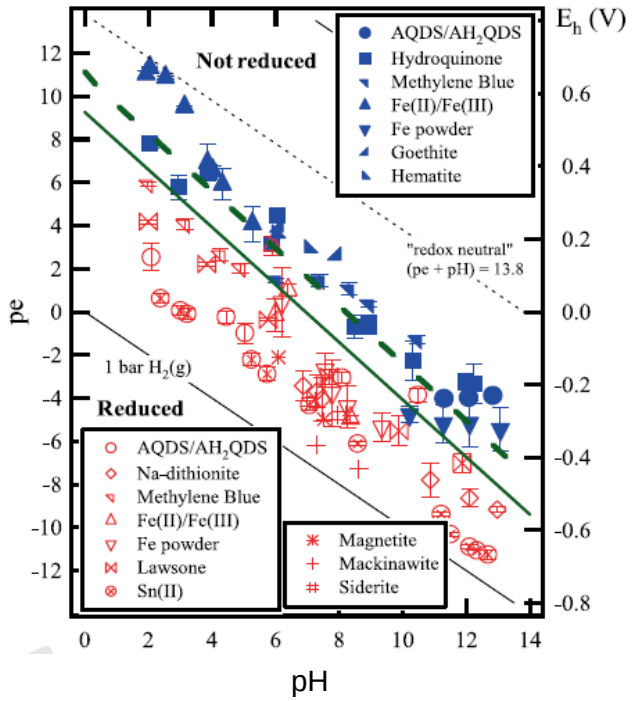

**Similar situation for anionic fission products:**

- **Se(-II), Se(0), Se(+IV), Se(+VI)**
- **$CH_4$ – $CO_3^{2-}$**
- **Tc(VII) – Tc(IV)**

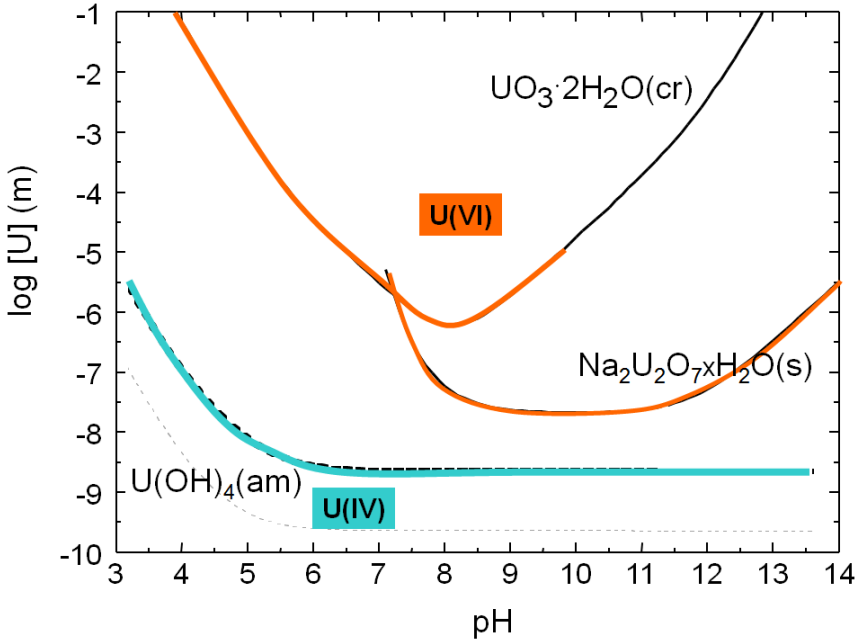
- Changes in redox state strongly impact RN chemistry and RN retention processes.
- FP7 RECOSY project offers valuable input for studies within CEBAMA.

# A) Redox reactions involving radionuclides

- *Radionuclide oxidation state, $E_h$ conditions*




**Tc(VII)** vs. immobile **Tc(IV)**




**U(VI)** vs. **U(IV)**

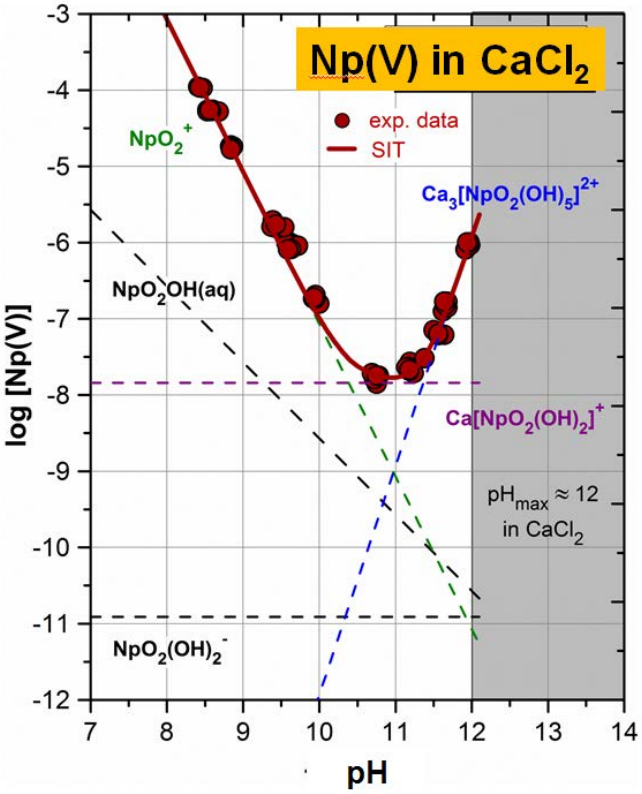
Need to assess redox processes and kinetics at hyperalkaline conditions

# B) Solubility and dissolution phenomena

- Prediction of reliable limiting RN solubility concentrations essential part of RN source term estimations.
- Precipitation/dissolution reactions significantly control RN retention.
- RN solubility evolves as function of geochemical boundary conditions
  - *Radionuclide oxidation state, $E_h$ + pH conditions*
  - *Main matrix solution components ($Na^+$, $Ca^{2+}$, $K^+$, …)*
  - *Complexing inorganic ligands ($OH^-$, $CO_3^{2-}$, $SO_4^{2-}$, [Si], …)*
  - *Complexing organic ligands (superplasticiser, cellulose degradation products, decontamination agents)*

# B) Solubility and dissolution phenomena

- *Main matrix solution components ($Na^+$, $Mg^{2+}$, $Ca^{2+}$, $K^+$, …)*




**EXAMPLE:**

- **Formation of new ternary species under certain conditions**
- **Impact on thermodynamics**
- **Potential impact on RN retentions**

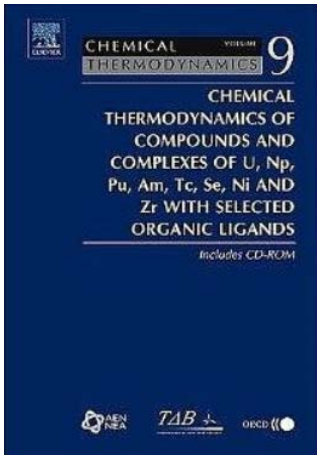
- Need to assess specific chemistry of $CaCl_2$ and KCl systems.
- Need to improve understanding of silicate complexation.

# B) Solubility and dissolution phenomena

- *Complexing organic ligands (superplasticiser, cellulose degradation products, decontamination agents)*

  Complexation of RN with organic ligands can impact RN behavior:

  - Changes in solubility
  - Changes in speciation and sorption
  - Changes in redox stability

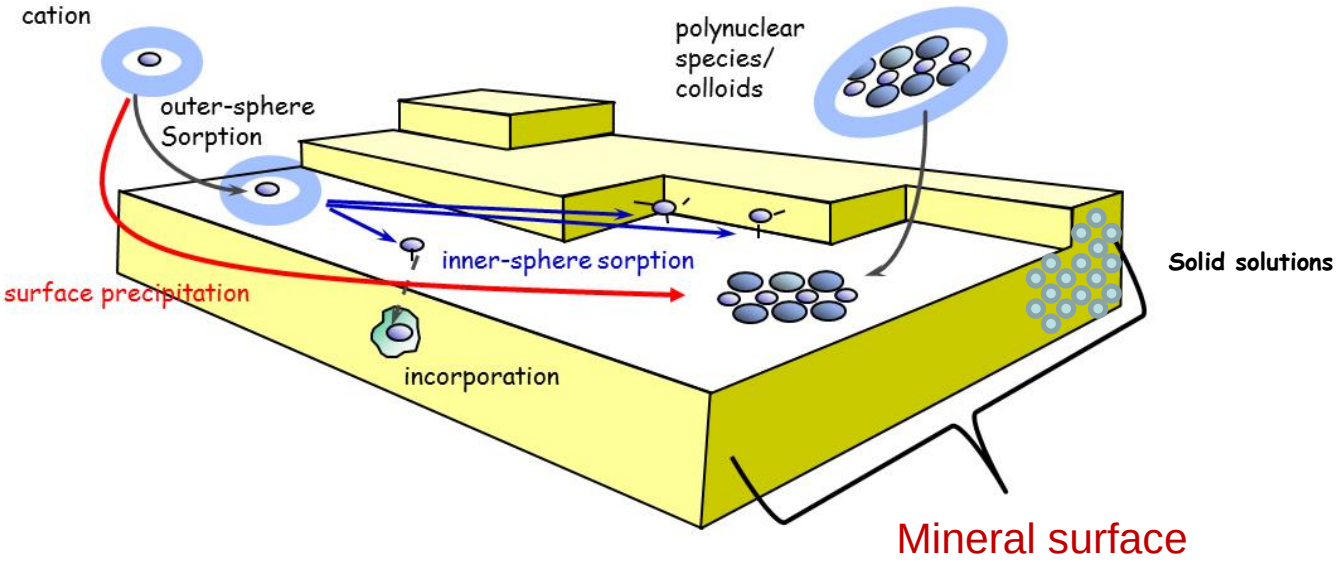



- *NEA-TDB volume offers detailed evaluation of selected organic ligands, however not complete in terms of ligand systems investigated!*
- *NEA-TDB activity to derive state-of-art-report on cement under preparation.*

Need to assess RN-organics interactions under relevant high pH conditions, including ternary systems like Ca-RN-org or RN-OH-org.

# C) Sorption and incorporation processes

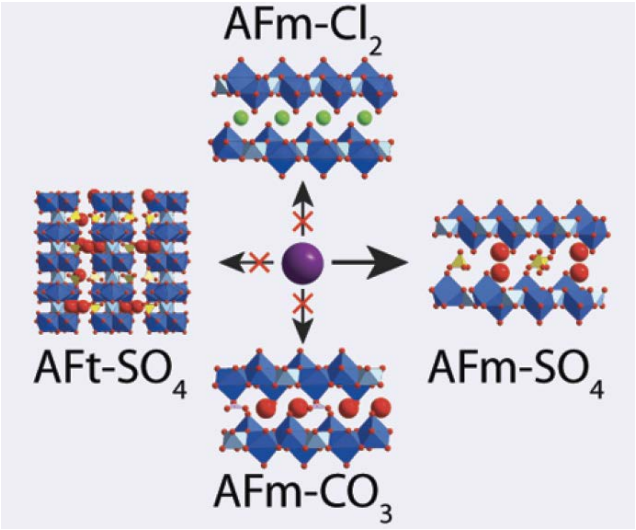
- Sorption processes on cement phases need to be addressed with priority as main retention processes for anionic fission products and actinides.




Need to derive advanced process understanding and models for RN sorption, assess impact of geochemical boundary conditions and complexants.

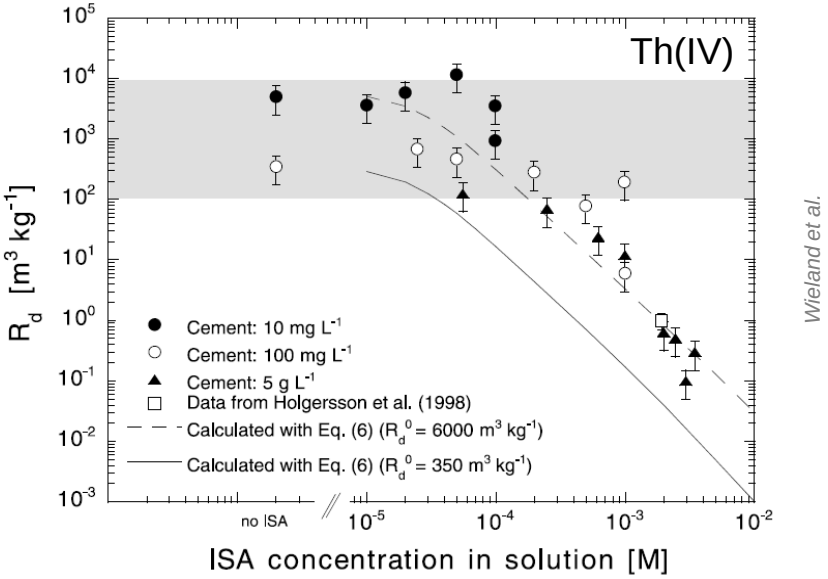
# C) Sorption and incorporation processes

- Examples: I-incorporation mechanism and impact of organics on sorption




Aimoz et al.

*Iodine uptake in AFm phases*




Wieland et al.

*Th(IV)-ISA cement interactions*

Need to derive advanced process understanding and models for RN sorption, assess impact of geochemical boundary conditions and complexants.

# CEBAMA: RN-Retention and Redox

- Many scientific investigations have been published in peer-reviewed journals or projects reports on RN behavior in cementitious systems.

- Several processes identified in the context of RN retention in cementitious environment which justify further dedicated investigations.

- R&D strongly profit from collaborative studies – synergies from coupling expertise on international level and performing joint research.

- Several potential project partner institutions in support of CEBAMA and dedicated Workpackage on RN retention (PSI-LES, BRGM, Amphos$^{21}$, SUBATECH, Loughborough Univ., KIT-INE)

# CEBAMA: RN-Retention and Redox

- Based upon present discussion, work in CEBAMA on RN retention and redox processes will include:
  - Redox reactions under high pH conditions (kinetics)
  - Investigation of RN solubility and complexation in pore solutions
    - *specific focus on organics*
    - *specific focus on silicate species ?*
  - RN sorption / desorption / incorporation impacting RN retention
  - Special focus on anionic species, investigation of Pu chemistry
  - RN interactions with specific waste types (to be further defined)

Karlsruhe Institute of Technology

EURATOM

safe solutions for radioactive waste

# *Thank you for your attention !!!*