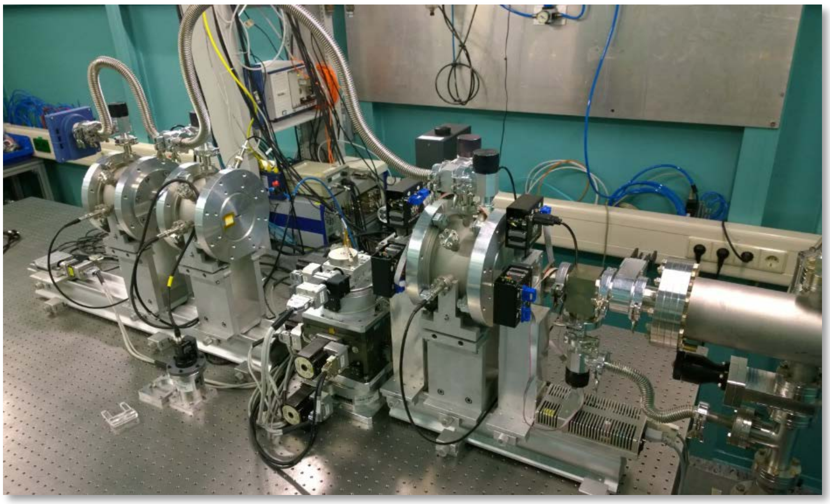
Masterarbeit Chemie / Physik am INE

Thema: Synchrotron beam induced speciation changes in XAFS studies of aquatic radionuclide systems

Background

Synchrotron based X-ray Absorption Fine Structure (XAFS) spectroscopy is one of the most powerful and versatile tools to determine the physicochemical state of potentially soluble radionuclide (actinide and fission product) species which might be released from a nuclear waste repository site in the case of (ground)water ingress. Although generally considered as a "non-destructive" technique, the resonant excitation of core electrons to unoccupied molecular orbital states in XAS (X-ray Absorption Spectroscopy) experiments and the following cascade of intra-molecular de-excitations leads to a rearrangement of the electronic structure, which might result in speciation changes (oxidation/reduction of the absorber atom, bond breaking to ligand atoms in complexes etc.). Additionally, formation of water radiolysis products ("radicals") in the ionizing, highly intense synchrotron beam might induce redox-reactions of redox labile radionuclide species.
INE operates two experimental stations for the investigation of radioactive materials at the KIT synchrotron radiation facility (KARA) on Campus North - the INE-Beamline (2005) and the ACT station at the new CAT-ACT beamline (2016) with a superconducting wiggler source. While examples for beam-induced speciation changes have been only sporadically observed at the older INE-Beamline (receiving photons from a conventional bending magnet source), experiments at the state of the art ACT station, offering two orders of magnitude more photon flux, seem to be generally prone to "radiation damage". How to avoid or minimize this phenomenon has not yet been investigated in a systematic manner.



Work description

For some selected aqueous systems (e.g., the Neptunium(IV) aquo-ion $Np(IV)_{aq}$, which tends to be oxidized to the trans-dioxo $Np(V)O_2^+$ cation in the presence of an intense synchrotron X-ray beam), beam induced speciation changes will be investigated by controlling and systematically changing the relevant experimental parameters:

- Metal cation concentration
- Total photon flux
- Photon flux density (focused/defocused beam)
- Sample temperature (from room to liquid nitrogen temperature)
- Exposure time to the beam
- Ground state electronic level (K- vs. L- / L- vs. M-edge)
- Conditions for recovery of the pristine state before irradiation

These investigations will include a precise determination of the beam induced temperature increase (deposited energy) in the sample vial ("beam damage" might be actually a temperature induced speciation change) as well as EXAFS studies of the effect of deep freezing on the "aqueous" speciation.

Methods:

- XAFS spectroscopy at well-defined conditions in transmission / fluorescence detection mode at the INE and ACT beamline stations (coop. INE beamline group)
- Sample preparation (coop. INE aquatic chemistry group)
- XAFS data analysis

Selected Publications:

- Rothe et al., The INE-Beamline for actinide science at ANKA, Rev. Sci. Instrum. 2012, 83(4): 043105. doi: 10.1063/1.3700813.
- Rothe et al., Fifteen Years of Radionuclide Research at the KIT Synchrotron Source in the Context of the Nuclear Waste Disposal Safety Case, Geosciences 2019, 9(2), 91. https://doi.org/10.3390/geosciences9020091

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