

XAFS investigation of fission and activation products in irradiated light water reactor fuels

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For several countries (e.g., Sweden, Finland or Germany) utilizing nuclear fission as energy source, the direct disposal of spent nuclear fuel (SNF) in a deep geological repository (DGR) for high active waste is the favored option for the back end of the nuclear fuel cycle. Regarding the long-term isolation of radiotoxic actinides or fission and activation products generated during in-reactor service of the fuel, various multi-barrier concepts are currently discussed. In general, the concepts envisage (i) a technical barrier, consisting of the irradiated fuel pellets inside their cladding tubes and a metallic container holding the fuel rod assemblies, (ii) a geotechnical barrier formed by construction materials of emplacement rooms and backfill materials retarding the ingress of solutions or - in case of the failure of the first barrier - retarding the release of radionuclides (RN) before reaching (iii) the geological barrier, i.e., the host rock surrounding the DGR and a possible overburden. As the initial barrier relevant for the potential release of RN from the DGR is the waste matrix (SNF and cladding) itself, precise information on SNF isotopic composition and RN speciation is of utmost importance in any safety analysis of the repository concept. While all actinide isotopes (^{238}U , unburned $^{235}\text{U}/^{239}\text{Pu}$ and all transuranic isotopes formed from ^{238}U by neutron capture and consecutive β -decay) tend to remain immobilized in a fluorite-type lattice as in pristine UOx (UO_2) or mixed oxide (MOX: $(\text{U,Pu})\text{O}_2$) fuel, certain highly mobile fission and activation product isotopes are of major concern for safety assessments due to their initial prompt release from the SNF matrices upon ground water contact (e.g., the cesium isotopes, ^{129}I as well as the activation product ^{36}Cl).

Reports on XAFS investigations of RN speciation in irradiated SNF samples are generally scarce, mainly focusing on the actinides [1,2], noble gases [3] or a few selected fission product elements, e.g. [4]. Research at the INE-Beamline and ACT stations of the KIT Light Source benefits from the unique proximity of hot cell lab facilities, where fragments of genuine nuclear waste forms (vitrified high active waste concentrates from reprocessing, SNF or cladding segments) can be conditioned, extracted and transported to the nearby beamlines for X-ray based speciation measurements (XAFS, HR-XANES, XRF, XRD). In this contribution we will focus on recent XANES measurements of the β -emitter ^{36}Cl , generated via neutron activation of impurities of the natural isotope ^{35}Cl in the cladding, the pristine fuel and adjacent construction materials, and the γ -emitting, long-lived fission product ^{129}I , both for the first time directly analyzed by XAFS as anionic species in SNF bulk fragments. Besides forming solid solutions with the original $\text{UO}_2/(\text{U,Pu})\text{O}_2$ lattice, some fission product cations with incommensurable ionic radii are expected to accumulate in separate oxide or perovskite-type phases in the SNF matrix, sometimes denoted as ‘grey phases’ (e.g., $(\text{Ba,Sr})(\text{U,Pu,Zr})\text{O}_3$). Those have been recently addressed by comprehensive Sr K-edge EXAFS measurements on a SNF bulk fragment and reference compounds.

[1] C. Degueldre et al., *J. Phys. Chem. Sol.* 75, 358–365 (2014).

[2] J. Rothe et al., *Geosciences* 9, 91 (2019).

[3] C. Degueldre et al., *Nuc. Instrum. Meth. in Phys. Res. B* 336, 116–122 (2014).

[4] E. Curti et al., *Environ. Sci.: Processes Impacts* 17, 1760–1768 (2015).