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XAFS investigation of a HAWC glass fragment issued from the Karlsruhe Vitrification Plant (VEK)

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The Karlsruhe Reprocessing Plant (WAK) was operated from 1971 to 1991 as a pilot facility for reprocessing of spent nuclear fuels from German pilot reactors and commercial power plants. Reprocessing activities resulted in ˜60 m3 of highly active waste concentrates (HAWC) stored on-site in liquid form. An important step in the current decommissioning of the WAK was the HAWC vitrification in the Karlsruhe Vitrification Plant (VEK) constructed close to the HAWC storage facilities [1]. Sections of genuine HAWC glass rods were retained during the vitrification process and transferred to the INE shielded box line for later glass product characterization. In 2013 a mm sized fragment with a contact dose rate of ˜590 µSv/h was selected and mounted in a specially designed sample holder for pilot XAS/XRF investigations at the INE-Beamline [2] located at the KIT synchrotron light source ANKA [3]. The experiment aimed at elucidating the potential of direct actinide / radionuclide speciation (with an emphasis on fission products) in highly active nuclear materials (e.g., waste glass, spent nuclear fuel) and assessing the possible influence of the γ-radiation field surrounding highly active samples on the XAS detection electronics.
While the influence of the γ-radiation field turned out to be negligible, initial radionuclide speciation studies by XAS were most promising. Exemplarily, normalized Se K- (left) and Tc K-edge XANES measurements of the HAWC glass fragment and corresponding Se and Tc reference samples were performed. Edge position and simple spectral fingerprint analysis point to the presence of Se in the glass as selenite oxoanion (SeO32-) as in Na2SeO3. Pronounced dampening of the near-edge fine structure indicates dispersion of the SeO32– oxoanions in the glass matrix, where the crystalline ordering such as in the Na2SeO3 reference is lost. Tc is dispersed as pertechnetate oxoanion (TcO4-) in the glass matrix as in the aqueous Tc(VII)/HClO4 reference sample, which is unequivocally proven by the edge shift relative to Tc(IV)O2 and the pronounced pre-edge feature at ˜21056 eV indicative of tetrahedral oxygen coordination.
Elemental X-ray lines were identified in the XRF spectra of the HAWC glass fragment recorded for different excitation energies using a five element LEGe fluorescence detector. In addition to Se and Tc discussed above and the plethora of elements contained in the glass fragment, the focus of these initial XAFS investigations was on the possibility for direct actinide speciation by recording corresponding L3 edge XAFS data. Th was not expected to be contained in the glass and, hence, was not detectable in XAFS scans across the Th L3 edge. Only a very tiny absorption signature was detected by scanning the energy across the Cm L3 edge. This signal was not sufficient to obtain any useful XANES data. This is in full agreement with the known composition of the HAWC oxide residue [1], where the Cm content is expected to reach about 1/10 of the Pu content, which, in turn, amounts to ˜1/30 of the U content of the HAWC glass. The concentrations of Am and Np are expected to reach twice the value obtained for Pu. For all actinide elements besides Th and Cm (U, Np, Pu, Am) as well as for Zr registration of high quality XANES data was possible - for some of these elements even reasonable EXAFS spectra were recorded. The XANES analysis reveals that uranium is present as U(VI), neptunium as Np(V), plutonium as Pu(IV), americium as Am(III) and zirconium as Zr(IV) in the HAWC glass.

[1] G Roth, S Weisenburger, Vitrification of high-level liquid waste: glass chemistry, process chemistry and process technology, Nucl. Engineering and Design 202, 197-207 (2000)
[2] J. Rothe, S. Butorin, K. Dardenne, M. A. Denecke, B. Kienzler, M. Löble, V. Metz, A. Seibert, M. Steppert, T. Vitova, C. Walther, H. Geckeis. The INE-Beamline for actinide science at ANKA. Rev. Sci. Instrum., 83, 043105 (2012)
[3] www.anka.kit.edu

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