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Neptunium characterization in uranium dioxide fuel: Combining a XAFS and a thermodynamic approach

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Because actinides (An) are typically accept various oxidation states, and because fuel redox conditions evolve with burn-up, others oxides than stoichiometric AnO2 are formed during irradiation.
In this work, neptunium chemical state and local environment in stoichiometric and oxidized (U0.9Np0.1)O2(+x) fresh samples were obtained by X-ray absorption spectroscopy at the NpLIII edge (17610 eV) at the ROBL beamline (ESRF). No variation of the white line position and intensity relative to NpO2 reference was evidenced, suggesting that Np remains tetravalent in all samples. However, since XANES NpLIII analysis was found to be ambiguous relative to Np+IV/V determination in humic solution (e.g. Denecke et al. 2004), the results were completed by EXAFS analysis. The EXAFS spectra did not reveal a short Np-O distance which would indicate the neptunly unit O=Np+V=O and corroborates as such the exclusive presence of Np+IV. Independently, the oxidation state of both actinides was predicted by a thermodynamic approach first considering separate phases (heterogeneous fuel), then ideal and non-ideal solid solution. The minimization of Gibbs energy was obtained by GEM-Selektor code developed at LES, NES, PSI, based on Gibbs energy values and molar heat capacities available in the literature for actinide oxides of interest (i.e. UO2, U4O9, U3O8, UO3, NpO2 and Np2O5). Thermodynamic modelling predicts the full reduction of NpO2+x into NpO2 and oxidation of UO2 in UO2+x, thereby confirming XAS observations.

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