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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  $AnO_2$  are formed during irradiation.

In this work, neptunium chemical state and local environment in stoichiometric and oxidized  $(U_{0.9}Np_{0.1})O_{2+x}$  fresh samples were obtained by X-ray absorption spectroscopy at the NpLIII edge (17610 eV) at the ROBL beam-line (ESRF). No variation of the white line position and intensity relative to  $NpO_2$  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 neptunyl 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.  $UO_2$ ,  $U_4O_9$ ,  $U_3O_8$ ,  $UO_3$ ,  $NpO_2$  and  $Np_2O_5$ ). Thermodynamic modelling predicts the full reduction of  $NpO_{2+x}$  into  $NpO_2$  and oxidation of  $UO_2$  in  $UO_{2+x}$ , thereby confirming XAS observations.

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