

## U/Pu M<sub>4,5</sub> edge HR-XANES investigations (i) of aqueous/colloidal Pu and (ii) at the Zircaloy cladding/spent nuclear fuel interface

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Compared to classical actinide (An) M<sub>4,5</sub>/L<sub>3</sub> edge XANES, high-energy resolution XANES (HR-XANES) provides significantly improved information on the actinide electronic structure and oxidation states [1-6]. We have investigated the speciation of (i) Pu in Pu colloids, and (ii) of U at the interface of spent nuclear fuel (SNF) and Zircaloy cladding material using the Pu and U M<sub>4,5</sub> edge HR-XANES spectroscopy technique. The spectra were recorded applying the Johann-type spectrometer installed at the CAT-ACT-Beamline at the KIT synchrotron radiation facility, Karlsruhe, Germany [7].

It is known that Pu(IV) has a high tendency for colloidal formation. The formation mechanism of the Pu(IV) colloids is still not well understood, strongly depends on the generation conditions and remains controversial. We will show that the Pu M<sub>4,5</sub> HR-XANES spectra for PuO<sub>2(cr)</sub>, PuO<sub>2(mcr)</sub> and Pu(IV)<sub>(aq)</sub> have characteristic fingerprints and allow to distinguish between Pu(IV) coordinated with O or OH/H<sub>2</sub>O. Based on these spectra, X-ray induced formation and agglomeration mechanisms of Pu(IV) colloids under the specific conditions of this study will be proposed. For the first time the Pu M<sub>5</sub> edge HR-XANES spectrum of PuO<sub>2</sub><sup>+</sup><sub>(aq)</sub> will be presented and compared to the spectra of Pu(IV)<sub>(aq)</sub> and PuO<sub>2</sub><sup>2+</sup><sub>(aq)</sub> as well as with computed partial density of states (An f -DOS) and HR-XANES spectra using the finite difference method (FDMNES code [8]) and the FEFF9 code [9].

The An speciation in SNF and especially in the interaction layer between the SNF pellet and the Zircaloy cladding material is still under discussion and may play a role for the mechanical behaviour of SNF under storage conditions notably if oxygen has access. We will illustrate that U with short trans-dioxo bonds (U(VI)O<sub>2</sub><sup>2+</sup>, uranyl) occurs onto the inner surface of a Zircaloy specimen, which was in contact with spent nuclear fuel. This Zircaloy specimen was sampled from a SNF fuel rod segment under air. U<sub>4</sub>O<sub>9</sub> however is the dominant U species on the inner surface of a Zircaloy specimen sampled from the plenum of the same SNF rod segment under air, too. U<sub>4</sub>O<sub>9</sub> contains U(IV) and U(V) and has a cubic structure very similar to UO<sub>2</sub>. It is a typical oxidation product on the surface of UO<sub>2</sub>/SNF at ambient conditions[10,11]. Uranyl formation has been observed to form only when exposing directly to liquid water or very high humidity [12,13]. Possible origin of these differences will be discussed.

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