

# **Np(V) uptake by the cladding corrosion product zirconia: a combined batch, spectroscopic, and modeling approach**

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When assessing the safety of a nuclear waste repository, the interactions of dissolved long-lived radionuclides, such as the actinide neptunium, with corrosion products in the near-field of the repository are crucial processes that have to be taken into account. Zirconia (ZrO<sub>2</sub>), the main corrosion product of the zircaloy cladding material of nuclear fuel rods, constitutes a first barrier against the release of radionuclides into the environment.

A multimethod approach was pursued to gain a thorough understanding of the Np(V) sorption processes on the water-zirconia interface. For the macroscopic description of the Np(V)-ZrO<sub>2</sub> system, pH-dependent batch sorption experiments (varying ionic strength, Np(V) concentration, and the solid-to-liquid ratio) as well as a sorption isotherm experiment at pH 6 were conducted. The uptake of Np(V) was pH-dependent, with an increased sorption starting from pH 3 and being at a maximum at pH 6 and above. The Np(V) sorption was independent of ionic strength, hinting to the presence of Np(V) inner-sphere complexes on the zirconia surface. This was supported by zeta potential measurements in the presence of neptunium, where a shift to higher pH values of the isoelectric point of the neat ZrO<sub>2</sub> was observed. The Np(V) sorption edge was shifted towards lower pH values with increasing solid-to-liquid ratio, indicating the presence of different kinds of sorption sites, which was also deduced from the shape of the sorption isotherm.

Molecular information of the surface species were obtained by Extended X-ray Absorption Fine Structure Spectroscopy (EXAFS) and *in situ* Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR-FTIR) revealing the predominant formation of inner-sphere Np(V) surface complexes. A short Np-Zr distance derived from EXAFS spectra suggested the presence of Np(V) bidentate complexes at the zirconia surface.

Reliable information about the number and denticity of surface species obtained by macroscopic and molecular spectroscopic investigations potentially facilitate modeling approaches such as surface complexation modeling (SCM) that in turn will contribute to a more profound prediction of the environmental behavior of neptunium.