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Np(V) uptake by zirconia (ZrO_2): a batch, spectroscopic, and modeling study

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The safety assessment of repositories for high-level radioactive waste, mostly spent nuclear fuel, requires a detailed understanding of the interactions of radionuclides with corroded phases in the near-field of a given repository. Zirconia (ZrO_2), 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 at the water−zirconia interface. For the macroscopic description, pH-dependent batch sorption experiments (varying ionic strength, Np(V) concentration, and solid-to-liquid ratio) as well as sorption isotherms experiments at pH 4.5 and 6.0 were performed. 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, suggesting the predominance of Np(V) inner-sphere complexes on the zirconia surface. This was supported by electrokinetic measurements in the absence and presence of neptunium, where Np(V) caused a shift to higher pH values of the isoelectric point of the neat ZrO_2. 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 (strong and weak), which was also corroborated by the shape of the sorption isotherms.

Molecular level information was derived from *in situ* attenuated total reflection Fourier-transform infrared spectroscopy and extended X-ray absorption fine structure spectroscopy (EXAFS), which confirmed the presence of Np(V) inner-sphere complexes. EXAFS experiments revealed the formation of a bidentate inner-sphere surface complex in the weak sorption site regime.

The derived information at the macroscopic and molecular levels was used to parametrize a charge distribution multi-site complexation (CD-MUSIC) model. The derived thermodynamic constants help to better predict the environmental fate of Np(V) in the context of nuclear waste repository assessments and support the appraisal of safety-relevant scenarios for the extended interim storage of spent nuclear fuel [1].

[1] I. Jessat et al., Unraveling the Np(V) sorption on ZrO_2: A batch, spectroscopic and modeling combined approach, *Journal of Hazardous Materials*, **2024,** 461, 132168.