

Characterization of the sorption behavior of trivalent actinides on zirconium(IV) oxide

M. Eibl, S. Virtanen,¹ S. Meriläinen,¹ J. Lehto,¹ T. Rabung,² N. Huittinen

¹University of Helsinki, Finland; ²Institute for Nuclear Waste Disposal, KIT, Karlsruhe, Germany

The uptake of trivalent Eu and Cm on zirconium(IV) oxide was investigated in batch sorption and TRLFS studies, respectively. Sorption of Eu^{3+} was found to start at a pH-value of 4. Based on TRLFS results, sorption of Cm^{3+} was assigned to occur through inner-sphere complex formation at the zirconia surface. A deconvolution of the TRLFS emission spectra gave three different sorption species with strong red-shifts of the peak positions (600.3 nm, 604.3 nm and 608.2 nm) compared to similar systems.

Zirconium(IV) oxide is a corrosion product of the zircalloy cladding material surrounding nuclear fuel rods.^[1] Therefore, studies involving interaction of actinides with ZrO_2 are necessary to enable predictions about the long term safety of final repositories for nuclear waste.

EXPERIMENTAL. In the batch sorption investigations, the sorption of 1×10^{-7} M and 1×10^{-5} M Eu^{3+} on 0.5 g/L and 5 g/L ZrO_2 was studied as a function of pH. The samples were separated by centrifugation at a relative centrifugal force of 4,025 and the Eu^{3+} concentration in the supernatant was measured with inductively coupled plasma mass spectrometry. The surface complexation and in situ speciation of 5×10^{-7} M Cm^{3+} in a 0.5 g/L ZrO_2 suspension at varying pH was investigated by TRLFS. All samples were prepared in a glove box under inert atmosphere (N_2 ; $\text{O}_2 < 0.1$ ppm). For the measurements, the samples were pipetted into cuvettes, which were sealed in the glove box. The laser system was a pulsed Nd:YAG (Continuum Surelite II or Powerlite Precision II 9020) pump laser coupled to a solid-state optical parametric oscillator (OPO, PANTHER EX OPO, Continuum). The excitation of Cm was carried out at 396.6 nm and the luminescence emission spectra were recorded 1 μs after the exciting laser pulse.

RESULTS. From the batch sorption experiments using Eu^{3+} as an actinide analogue, sorption can be seen to occur already at a pH-value of approximately 4.0–4.2 depending on the metal ion concentration used in the experiments. Complete sorption is reached at approximately pH 5.3 in both cases (Fig. 1).

The emission spectra obtained in the TRLFS measurements show a deviation from the aquo ion starting at pH 4.0, im-

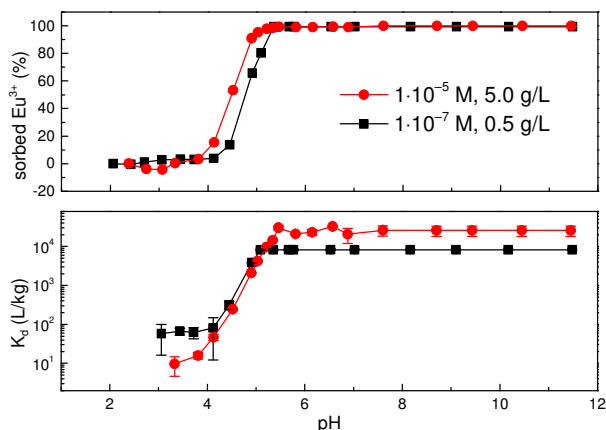


Fig. 1: Batch sorption curves for Eu^{3+} on ZrO_2 plotted as sorption percentage (top) and as sorption distribution coefficient, K_d (bottom).

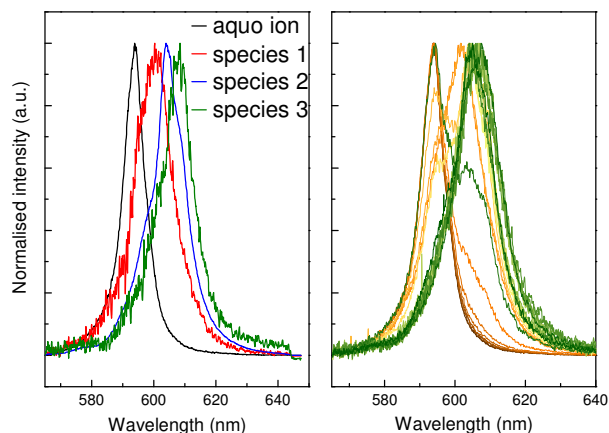


Fig. 2: Deconvoluted species from sorption experiments of 5×10^{-7} M Cm^{3+} on 0.5 g/L ZrO_2 (left) and emission spectra from the sorption experiments in the pH-range from 3.0 to 10.8 (right).

plying that inner-sphere sorption occurs on the ZrO_2 surface. A deconvolution of the spectra collected at various pH values (3.0–10.8) reveals three different pH-dependant species on the ZrO_2 surface showing peak positions at 600.3 nm, 604.3 nm and 608.2 nm (Fig. 2).

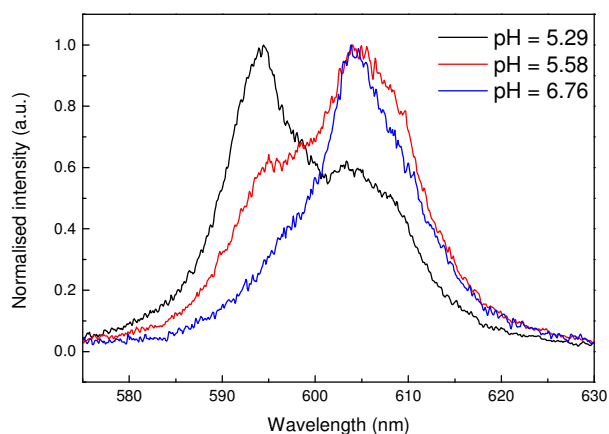


Fig. 3: Selected emission spectra from sorption species of 5×10^{-7} M Cm^{3+} on 0.5 g/L ZrO_2 .

The red shift of the two latter species is very large in comparison to Cm^{3+} surface complexes found on other oxide minerals such as corundum or $\gamma\text{-Al}_2\text{O}_3$.^[2, 3] In addition, a closer look on the emission spectra shows a red shifted shoulder in the pH-region between 5 and 6 which disappears with increasing alkalinity (Fig. 3).

Therefore, it is not clear whether the identified sorption species can be explained only by the adsorption of Cm^{3+} hydrolysis complexes with increasing pH as done in previous studies on Cm^{3+} sorption onto oxide minerals^[2, 3] or whether a different retention mechanism has to be considered. Thus, further investigations need to be done for a complete understanding of the surface sorption processes on the ZrO_2 system.

[1] Cox, B. (2004) *J. Nucl. Mater.* **336**, 331–368.

[2] Rabung, T. et al. (2006) *Radiochim. Acta* **94**, 609–618.

[3] Kupcik, T. et al. (2016) *J. Colloid Interface Sci.* **461**, 215–224.