Characterization of Gorleben Humic Colloids and Sensitivity of NEXAFS Spectroscopy on Actinide Sorption Kinetics

T. Schäfer (SUNY, Stony Brook; Forschungszentrum Karlsruhe, INE), R. Artinger, A. Bauer (Forschungszentrum Kalrsruhe, INE), S. Wirick and C. Jacobsen (SUNY, Stony Brook)

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Introduction: Colloidal facilitated groundwater transport might enhance the mobility of environmental critical substances including radionuclides. For risk assessment analysis it is essential to understand the sorption as well as the kinetic processes involved with actinides/humic colloid interaction to estimate the potential long-term mobilization of radiotoxic elements in the far-field of a repository site. Groundwater samples for further investigation were taken from the Gorleben site (Lower Saxony, Germany), which is one of the sites under investigation as a possible nuclear waste repository for high level nuclear waste. At the site, sandy sediments with high permeability are found above the Permian salt dome, with local dissolved organic carbon (DOC) concentration ranging up to 200 mg/L (Artinger *et al*., 2000). Laboratory scale migration experiments observed an increase in the recovery of the trivalent actinide Americium with increasing contact/equilibrium time to humic colloids prior to injection (Artinger *et al*., 1998). To elucidate the process responsible for the observed change in sorption reversibility soft X-ray spectrosmicroscopy was used as a chemical binding sensitive method.

Methods and Materials: Groundwater samples of the Gorleben site with DOC concentrations from 1.1 to 81.9 mg/L were analyzed by C K-edge XANES measurement in the energy range from 275 to 310 eV. Due to the complexity of the humic substances, point spectra were avoided and spectra generated using large area scans by analyzing images obtained by the software implemented stack mode. All measurements are conducted in a wet cell to prevent dehydration artifacts. Beside untreated humic colloids, batch samples of kinetic experiments with various Eu concentration (1E-4 to 1E-7 mol/L) and contact time (1 day to 1 year) were investigated in the identical way. These kinetic analysis are compared with sorption experiments including well defined functional groups as phthalic acid, ascorbic acid or poliacrylic acid.

Results: The XANES analysis of the pure humic groundwater colloids in GoHy-532 and GoHy-2227 with 69-79% humic acid content (Artinger et al., 2000) observed comparable features, whereas changes in the 1s C NEXAFS are visible in GoHy-412 and GoHy-182 (44-67% hydrophilic acids). (**Figure 1**) A decrease in peak height at the resonance of the C_6H_6 π^* bond around 285 eV and an increase in the resonance at the C=O π^* bond near 287 eV could be observed. The kinetic studies of Eu sorption on GoHy-2227 (88.1mg/L DOC) showed a less pronounced shoulder at 287.5 eV (C-H* resonance) with Eu sorption (**Figure 2**). Furthermore the σ^* resonances showed a significant shift from 293 eV (C-O σ^* resonance at 293 eV and C-C σ^* resonance at 292 eV) to 300 eV after 42d contact time, indicating a binding length change for C-C or C-O bonds (**Figure 2**). The intensity differences of C=C π^* and σ^* resonances in the spectrum after 42d reaction time might be related to possible aggregation by local charge neutralization changing the molecular weight and therefore the concentration of C=C π^* bonds.

Conclusions: The XANES investigations observed differences in the functional group content of mobile groundwater colloids of the site Gorleben. Additionally we could show in this ongoing research, that C K-edge XANES investigations are capable to resolve time dependent changes of metal (including radiotoxic metal) sorption on humic substances. These results indicate that the observed reversibility changes of trivalent actinide/lanthanide sorption are related to structural changes in the humic colloids resulting in a shift of the binding length and/or binding type as well as the density of molecular structure.

References: Artinger *et al*., *J. Contam. Hydrol.*, **35**,261-275, 1998; Artinger *et al*., *Appl. Geochem.*, **15**, 97-116,2000.

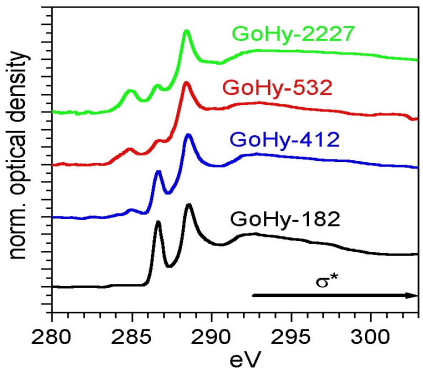

Figure 1. C K-edge XANES of investigated Gorleben groundwater humic colloid samples

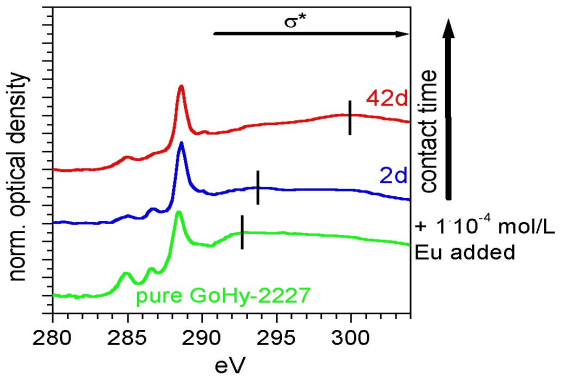

Figure 2. Time dependent changes in C K-edge XANES of Gorleben groundwater GoHy-2227 colloids after addition of $1 \cdot 10^{-4}$ mol/L Europium (pH 8.65)