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Soft X-Ray Spectromicroscopy Investigation of Humic Acid Aggregates

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Beamline(s): X1A

Introduction: Colloidal stabilization of contaminants is regarded as key factor for the assessment of radionuclide migration in the geosphere. Colloid-borne actinides can be mobile in groundwaters and thus enhance radionuclide transport from a nuclear waste repository. Organic and inorganic 'carrier colloids' as well as radionuclide 'eigencolloids' play a role in the underlying mobilization/immobilization processes. Aqueous humic substances (HS) form natural organic colloids with high affinities for metal cation complexation. Whereas investigations of actinide binding properties of humic acids (HA) implicate carboxylate groups as the primary functional groups complexing metal ions, variations in the morphology of colloidal sorbents are thought to influence their metal affinities.

Methods and Materials: Soft x-ray spectromicroscopy investigations of aqueous colloid suspensions are performed using the scanning transmission x-ray microscope at NSLS beamline X1A ('outboard-STXM'), operated by SUNY. All samples are investigated as aqueous suspensions enclosed in silicon nitrate wet cells. C K-NEXAFS spectra are extracted from STXM image stacks. Samples containing groundwater HS as well as purified Aldrich HA (AHA) are investigated. In the present studies, Eu(III) serves as a homologue for trivalent actinides. HS/HA aggregates and mixed organic/inorganic agglomerates formed following addition of Eu(III) cations, hydrous ferric oxide (HFO) and Eu(III) (hydr)oxide colloids to HA solutions are analyzed. Additionally, simple organic acids are investigated as reference compounds for HS macromolecules (Fig. 1).

Results: STXM micrographs of Eu-humates reveal zones of different morphologies and optical densities. In the case of purified AHA, C K-NEXAFS spectra indicate the segregation of different HA fractions with varying contents of functional groups. This is possibly due to humic species with different affinities for metal cation complexation. The Eu(III) distribution within these agglomerates cannot be unambiguously deduced from their C K-NEXAFS spectra. However, as we observe when comparing fresh samples to samples aged for several months, the density of these aggregates increases with time. HS aggregation induced by pH-decrease, addition of Eu(III) cations and sorption onto HFO or colloidal Eu(III)-(hydr)oxide all lead to different pronouncement of the spectral resonances commonly associated with different functional groups (Fig. 2).

Conclusions: Natural groundwater HS as well as purified AHA appear as chemically heterogeneous organic compounds. HA interaction with different inorganic colloids as well as variation of solution parameters (addition of metal cations, ionic strength and pH variations) leads to morphological and chemical changes visible in soft x-ray micrographs and C K-NEXAFS spectra. STXM measurements, including suitable reference compounds, promise to further our understanding of these heterogeneous systems.

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References: M. Plaschke, J. Rothe, T. Schäfer, M. A. Denecke, K. Dardenne, S. Pompe, and K.-H. Heise, "Combined AFM and STXM in situ study of the influence of Eu(III) on the agglomeration of humic acid", *Colloids and Surfaces A* (2001), in print.

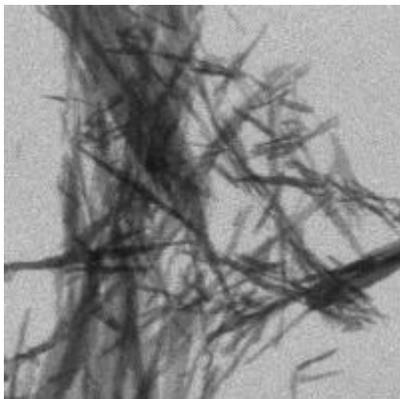


Fig. 1 STXM micrograph of isophthalic acid crystals at 290 eV ($20 \times 20 \mu\text{m}^2$).

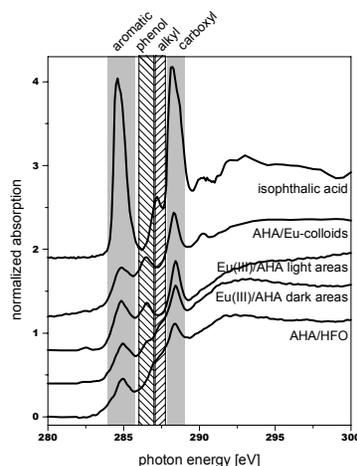


Fig. 2 C K-NEXAFS derived from different AHA agglomerates and isophthalic acid.