



STXM / NEXAFS investigation of humic acid metal cation interaction

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Waste matrix dissolution following water intrusion in a future underground nuclear waste repository is regarded as a possible failure scenario leading to the dispersal of radioactive substances in the environment. Dissolved actinides, carriers of the long term radiotoxicity, may interact with groundwater constituents or sediment and host rock phases. These processes can either enhance or retard actinide mobility in the aquifer surrounding the repository. Actinide species may be highly mobile occurring as 'eigen-colloids' or actinides adsorbed on groundwater colloids. The latter include dissolved humic acids (HA), mineral particles like iron oxides/hydroxides or clays and mineral/organic associations. The chemical characterization of these carrier colloids and a molecular scale understanding of the actinide-colloid interaction is a prerequisite to reliable prediction of actinide mobility based on model calculations. Therefore, chemical speciation information along with micro-scale morphology information is mandatory. Scanning Transmission X-ray Microscopy (STXM) is a powerful technique to reveal the chemical functionality and morphology of organic matter on a sub- μm scale. Moreover, STXM benefits from the ability to characterize organic samples in a thin film of aqueous solution. Morphological and microchemical information can be obtained at the same time within the spectral 'water window' (i.e., between the C 1s and O 1s absorption edges at 284 eV and 537 eV, respectively). This ensures that complex hydrated structures of HA are kept in their native state. STXM investigations of HA in contact with polyvalent metal cations are carried out at the NSLS and SLS endstations. STXM micrographs at the carbon K-edge of metal cation loaded HA show optically dense zones (densification of carbon) embedded in a matrix of less dense material. Carboxyl groups are proposed to act as the primary HA cation attachment sites. NEXAFS (Near Edge Absorption Fine Structure) spectra of the segregated metal cation/HA fractions exhibits a distinct complexation effect in the HA dense zones: a strong decrease of the carboxyl transition intensity is accompanied by the appearance of a new absorption feature at slightly lower energy adjacent to the carboxyl resonance. This interpretation is confirmed by comparison to similar observations obtained for metal ion complexes of polyacrylic acid used as a reference compound. Quantum chemical calculations show that the extent of the energy shift is primarily dependent on the metal cation and the resulting complex geometry. By laser scanning luminescence microscopy we were able to demonstrate that metal cations (e.g., Eu(III)) are enriched in the HA optically dense zones. These zones presumably consist of HA fractions with increased amounts of complexing sites, thus playing a dominant role in the colloid mediated transport of actinides or lanthanides in aquatic systems.

References:

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