

Speciation of Actinides by Time-resolved Laser Fluorescence Spectroscopy

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Abstract. Spectroscopic actinide speciation, providing fundamental information on processes on a molecular scale, is essential for performance assessment of nuclear waste repositories and useful for development of partitioning strategies. Time-resolved laser fluorescence spectroscopy (TRLFS) is a sensitive speciation technique, which allows actinide characterization and quantification without disturbing the chemical equilibrium. Cm(III) has excellent fluorescence properties and thus can be used as a representative for the trivalent actinides in speciation studies down to the nanomolar range. TRLFS provides information on the structure of An(III) complexes and can be applied not only to solutions but also to solids and suspensions. In this presentation examples of the application of TRLFS for actinide speciation in research issues related to nuclear waste disposal and partitioning are given:

a) In order to model the aqueous speciation of actinides in aquatic systems, fundamental knowledge of the participating chemical reactions and the corresponding thermodynamic data are needed. In the past few years considerable progress in establishing a thermodynamic database for lanthanides and actinides has been achieved. However, most of the available data are restricted to temperatures near 20°C. Depending on the disposed waste and the surrounding technical and geological barrier, the temperature in the direct vicinity of the repository can reach up to 200°C. Therefore, it is necessary to determine stability constants and thermodynamic data at elevated temperatures. A high temperature and high pressure cell for TRLFS has been developed and applied to study complexation reactions with various organic and inorganic ligands in the temperature range from 20-200°C. The results show that TRLFS is a powerful method to obtain thermodynamic data at elevated temperatures crucial for a reliable description of the migration behaviour of trivalent actinides (An(III)) in the near field of a nuclear waste repository.

b) Partitioning may be used to isolate long-lived radionuclides from nuclear fuel reprocessing waste for subsequent transmutation to shorter lived or stable nuclides, or for their conditioning and immobilization in special matrices for disposal. The separation of trivalent actinides (An(III)), namely Am(III) and Cm(III), from lanthanides (Ln(III)) is a key step in the partitioning & transmutation (P&T) strategy. The chemical properties and the ionic radii of An(III) and Ln(III) are comparable, rendering high demands on the selectivity of the extraction ligand in liquid/liquid extraction processes. Various soft N-donor ligands have been developed, which extract An(III) selectively over Ln(III) from nitric acid solutions into the organic phase with separation factors for Am(III) or Cm(III) vs. Eu(III) of > 100. Our research focuses on attempts to understand the underlying reason for the partitioning ligand selectivity. TRLFS is used for determination of coordination structures and thermodynamic data for Cm(III) complexed with various N-donor ligands and comparison to those of their Eu(III) counterparts. The results are of particular importance to optimize partitioning ligand design and, hence, extraction performance.