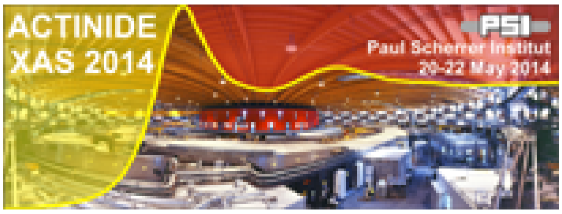
Actinide XAS 2014



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In situ XAFS measurement of uranyl-amide complexes under Xe-lamp irradiation

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In our group, an innovative chemical separation process is proposed for the recovery of all actinide from spent nuclear fuel. One of the main purposes of this process is selective isolation of uranium with branched alkyl type N,N-dialkyl-monoamide(BAMA) and the other is all actinide recovery with hetero donor ligand, phenathroline amide, which composed oxygen and nitrogen atoms.

Since BAMA has the steric hindrance on the complexation with metal cations, BAMA can be used to separate An(VI) from An(IV). One of BAMA, N,N-di-(2-ethyl)hexyl-(2,2-dimethyl)propanamide (D2EHDMPA), can recover U(VI) selectively without accumulating Pu(IV) in uranium isolation process. From the results of uranium extraction in the presence of neptunium, D2EHDMPA can extract and separate U(VI) from Np(VI) without reduction from Np(VI) to Np(V) or Np(IV). Furthermore, D2EHDMPA could not extract fission products like technetium in the presence macro amount of uranium.

The structural parameters of uranium(VI)-BAMA were determined by EXAFS to elucidate the mechanism of selective separation of uranium(VI). EXAFS measurements of uranium(VI) and thorium(IV)-BAMA complexes were performed at the BL-11XU of SPring-8. Uranium(VI) and thorium(IV)-BAMA complexes were measured by transmission mode. Ligands used structural analysis were N,N-dioctylbutanamide(DOBA) and D2EHDMPA for U(VI) and Th(IV). Uranium(VI) and thorim(IV)-BAMA samples for EXAFS measurement were prepared by solvent extraction method using n-dodecane as diluent and by synthesis in ethanol solution. The obtained bond distance between uranium(VI) and oxygen of N,N-dialkyl monoamide are 2.39 Å for DOBA, and 2.31 Å for D2EHDMPA. Bond distances of U-O (O=C; amides) were changed dependence on amides structure, especially carbonyl alkyl group branching on α-position.

In case of Th(IV)-D2EHDMPA complex in ethanol, D2EHDMPA could not coordinate with Th(IV). The components of first coordinate sphere of Th were oxygen atoms of four nitrate anions and water molecules. The U(VI) isolation manifested only in branched alkyl amide (BAMA) extraction system. The bulky D2EHDMPA extractant could not solvate tetra valence cation like Th and Pu because of steric effects of nitrate ions which already coordinated Th and Pu cation.

In the presentation, we will show the results of in situ XAFS measurement of U-amide (and/or TBP) complexes on uranium valence change by Xe-lamp irradiation in order to evaluate U(VI) selectivity.

Primary author: Dr SUZUKI, Shinichi (Japan Atomic Energy Agency)

Presenter: Dr SUZUKI, Shinichi (Japan Atomic Energy Agency)

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