 ROBL-CRG	Experiment title: Investigation of the competing reaction between hydrolysis of U(IV), Th(IV), Zr(IV) and Ce(IV) and ligation by carboxylic groups	Experiment number: 20-01-725
Beamline: BM 20	Date of experiment: from: 29/10/2012 to: 30/10/2012	Date of report: 18/01/2013
Shifts: 3	Local contact(s): Christoph Hennig	<i>Received at ROBL:</i> 18/01/2013
Names and affiliations of applicants (* indicates experimentalists): Christoph Hennig, Stephan Weiss Helmholtz-Zentrum Dresden-Rossendorf, Institute of Resource Ecology, Bautzner Landstrasse 400, 01314 Dresden Germany		

Report:

The hydrolysis of U(IV), Th(IV), Zr(IV) and Ce(IV) results usually in more or less stable colloids. The formation of such colloid particles has to be distinguished from the carboxylates complexes. We report here on results obtained in a Th(IV) colloide system [1]. Comparative studies on carboxylates are planned for further experiments within this project.

Th/silica colloids were prepared by rapid dilution of thorium carbonate in silicic acid solution. Solutions with silicic acid concentrations below and above the silica solubility limit of of 2×10^{-3} M were prepared to obtain both monomeric as well as polymeric silicic acid species. Immediately after adding the silicic acid to the thorium carbonate solution, a strong increase of scattered light intensity was observed as shown in Fig. 1, indicative of the formation of colloids. The scattering intensity of a suspension containing colloids with a molar Si/Th ratio of 2.14 at pH 7 drops down within 32 days followed by sedimentation of the precipitate. A suspension with the same molar Si/Th ratio at pH 8 shows an increased colloid stability. A colloid suspension with a molar Si/Th ratio of 2.93 is stable at pH 7 over nearly one year.

EXAFS spectra of the colloid samples show silicon atoms in the environment of thorium with a Th-Si distance of ~ 3.25 Å (Fig. 2). This short distance is characteristic for silica in bidentate coordination and reveals coordination of Th and silica. High-energy X-ray scattering indicate in addition short Th-Th distances of 3.98 Å. The colloid structure is not homogenous. To clarify this issue, the bulk Si/Th ratio of the colloids, determined by ICP-MS, and the surface Si/Th ratio, determined by X-ray

photoelectron spectroscopy (XPS), were compared. XPS is a surface sensitive technique with an excitation depth of 5-10 Å. The size of such colloids is < 20 nm. Samples with low Si/Th ratios show a good agreement between the volume and the surface composition. In contrast, a sample with a Si/Th ratio of 1.45 in the volume reveals, when tested by with XPS, a Si/Th ratio of 2.77. This indicates an enrichment of silica at the colloid surface. The enrichment of silica at the particle surface is most likely related with the reaction kinetics. Th shows a fast kinetics and polymerizes in the first minutes of the reaction with Th and/or Si. With decreasing Th concentration the reaction kinetics becomes slower and is determined by the kinetics of silicic acid and oligomeric silica species. The light scattering measurements show fast initial formation of colloids, determined by polymerization of Th. Subsequently, the scattering light intensity increases slowly and reaches a steady state after ~7 days. Further Th polymerization is most likely limited by silica enrichment at the particle surface.

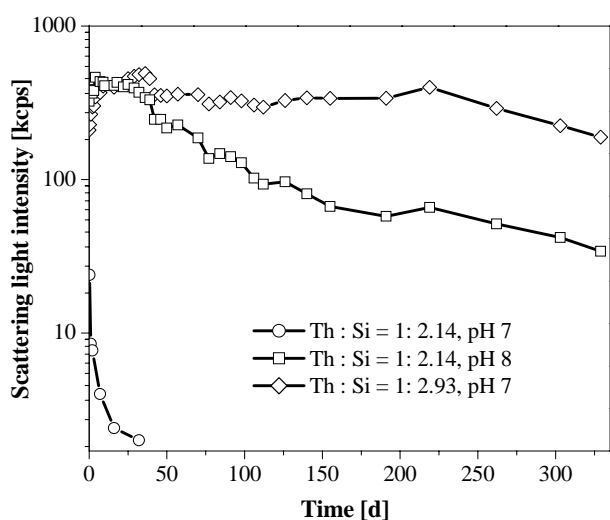


Fig. 1: Long-term stability of the Th/silica colloids. Initial [Th] = 0.8 mM, [HCO₃⁻] = 50 mM.

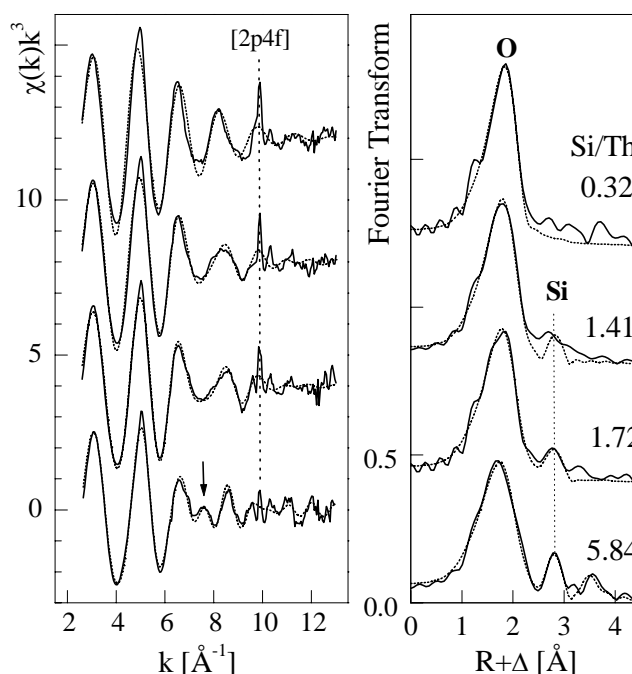


Fig. 2: Thorium L₃ edge EXAFS (left) and their corresponding Fourier transform (right) of colloid samples with Si/Th ratios noted in the figure.

REFERENCE

- [1] C. Hennig et al. Solid-state properties and colloidal stability of thorium(IV)-silica nanoparticles *Geochim. Cosmochim. Acta* **103** (2013) 197-212.