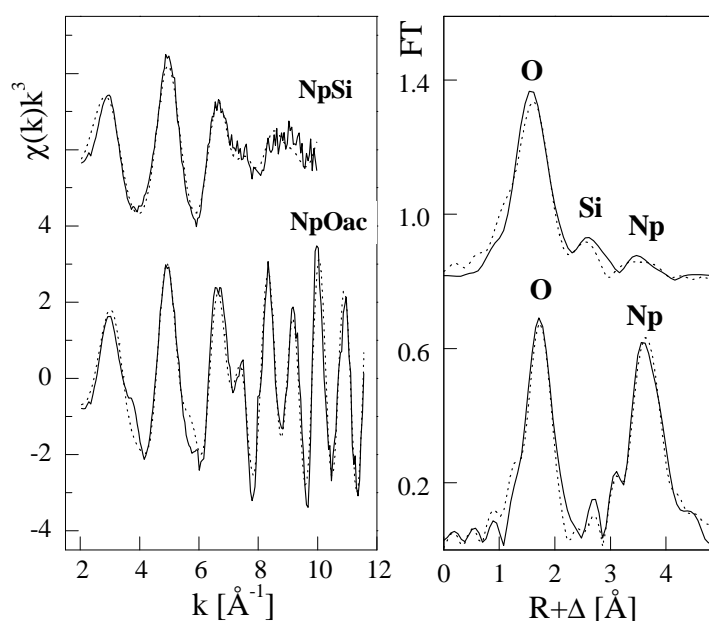
 ROBL-CRG	<b>Experiment title:</b> EXAFS-investigations on Np(IV) silicates	<b>Experiment number:</b> 20-01-724
<b>Beamline:</b> BM 20	<b>Date of experiment:</b> from: 03. 11. 2012                      to: 06. 11. 2012	<b>Date of report:</b> 02. 02. 2017
<b>Shifts:</b> 9	<b>Local contact(s): Christoph Hennig</b>	<i>Received at ROBL:</i> 02. 02. 2017
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## Report:

The reducing conditions in a nuclear waste repository render neptunium tetravalent. Thus, Np is often assumed to be immobile in the subsurface. However, tetravalent actinides can also become mobile if they occur as colloids. This experiment has shown that Np(IV) is able to form silica-rich colloids in solutions containing silicic acid at concentrations of  $2 \times 10^{-3}$  M where silicic acid is expected to start polymerization. These Np(IV)–silica colloids have a size of only a few nanometers and can reach significantly higher concentrations than Np(IV) oxyhydroxide colloids in absence of silica. The colloids under discussion can be stable in the waterborne form over longer spans of time. In the Np(IV)–silica colloids, the actinide–oxygen–actinide bonds are increasingly replaced by actinide–oxygen–silicon bonds due to structural incorporation of Si atoms.

Investigations of the structure of the nanoparticles were performed with EXAFS spectroscopy [Fig. 1]. The spectra were collected in the fluorescence mode. The aqueous colloid solution (Sample **NpSi**) was measured at ambient temperature. As reference a sample of Si-free Np(IV) oxyhydroxide was prepared by precipitation of Np(IV) from a Np(IV) solution in 1 M HNO<sub>3</sub> using NaOH. This precipitate (Sample **NpOac**) was measured in a closed-cycle He cryostate at 15 K.

The Fourier transform (FT) of the EXAFS spectrum of sample **NpOac** shows an oxygen shell with a large Debye–Waller factor of  $0.012 \text{ \AA}^2$  and a well pronounced Np peak. The large Debye-Waller-factor of the oxygen atoms indicates different Np–O distances, although they cannot be resolved due to the limited  $k$  range. The spectrum is equivalent to that of similarly prepared Th(IV) oxyhydroxides [1] and can be regarded as  $[(\text{Np},\text{Si})\text{O}_n(\text{OH})_{4-n} \cdot x\text{H}_2\text{O}]^{4-2n-(4-n)}$ . The spectrum of the colloidal particles in sample **NpSi** exhibits a strong dampening of the EXAFS oscillation, related to a peak broadening in the FT and an even larger Debye–Waller factor. These spectral features indicate a significant disorder in the colloid structure. A small peak occurs in the FT which indicates silicon atoms with a Np–Si distance of  $3.11 \text{ \AA}$ . This short Np–Si distance is characteristic of silica in bidentate coordination, while monodentate coordination would result in a significantly longer Np–Si distance. A small but less specific peak at a larger distance seems to indicate Np–Np interactions. It follows that, as for U(IV)–silica colloids and Th(IV)–silica colloids [1] also in the case of Np(IV)–silica colloids the An–O–An bonds are increasingly replaced by An–O–Si bonds, which means that silica is included into the structure of the solid  $[(\text{Np})\text{O}_n(\text{OH})_{4-n} \cdot x\text{H}_2\text{O}]^{4-2n-(4-n)}$  if the solution contains silicic acid.



**Fig. 1** Np  $L_3$  edge EXAFS spectra (left) and their corresponding Fourier transforms (right) of a colloid sample  $[(\text{Np},\text{Si})\text{O}_n(\text{OH})_{4-n} \cdot x\text{H}_2\text{O}]^{4-2n-(4-n)}$  in aqueous solution with 1 mM Np(IV) and 3 mM Si in 0.1 M  $\text{NaHCO}_3$  (Sample **NpSi**), and a precipitate of  $[(\text{Np})\text{O}_n(\text{OH})_{4-n} \cdot x\text{H}_2\text{O}]^{4-2n-(4-n)}$  under acidic conditions (Sample **NpOac**).

Possible implications of the formation of such colloids for environmental scenarios are discussed in the articles related with these measurements [1-3].

[1] Hennig, C., Weiss, S., Banerjee, D., Brendler, E., Honkimäki, V., Cuello, G., Ikeda-Ohno, A., Scheinost, A.C., Zänker, H. Solid-state properties and colloidal stability of thorium(IV)-silica nanoparticles *Geochim. Cosmochim. Acta* **103** (2013) 197-212.

[2] Husar, R., Weiss, S., Hennig, C., Hübner, R., Zänker, H. Formation of neptunium(IV)-silica colloids at near-neutral and slightly alkaline pH. *Environmental Science & Technology* **49** (2015)1, 665-671.

[3] Husar, R., Hübner, R., Hennig, C., Martin, P. M., Chollet, M., Weiss, S., Zänker, H., Stumpf, T., Ikeda-Ohno, A. Intrinsic formation of nanocrystalline neptunium dioxide under neutral aqueous conditions relevant to deep geological repositories. *Chemical Communications* **51** (2015), 1301-1304.