

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

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- 1st March for experiments carried out up until June of the previous year;
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Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	Experiment title: Neptunyl adsorption to calcite	Experiment number: 20-01 687
Beamline: RoBL	Date of experiment: from: 05.02.2009 to: 06.02.2009	Date of report: 13.10.2009
Shifts: 2	Local contact(s): Andreas C. Scheinost	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): *Frank Heberling Institut für Nukleare Entsorgung Karlsruher Institut für Technologie (Forschungszentrum Karlsruhe) Hermann von Helmholtz Platz 1 76344 Eggenstein Leopoldshafen		

Report:

Neptunyl, Np(V)O_2^+ , along with the other actinyl ions U(VI)O_2^{2+} and $\text{Pu(V,VI)O}_2^{(+,2+)}$, is considered to be highly mobile in the geosphere, but may be retained by interactions with mineral surfaces (inner- or outer-sphere adsorption, ion-exchange, coprecipitation/structural incorporation). Detailed information about the exact mechanisms including the structure and stoichiometry of the adsorption complexes is crucial to predict the retention behavior in diverse geochemical environments. Here, we investigated the structure of the neptunyl adsorption complex at the calcite-water interface at pH 8.2 in equilibrium with air by means of low temperature (15 K) EXAFS spectroscopy at the Np-L3 edge. The coordination environment of neptunyl consists of two axial oxygen atoms at $1.87(\pm 0.01)\text{Å}$, and an equatorial oxygen shell of six atoms at $2.51(\pm 0.01)\text{Å}$. Two carbon backscatterers at $2.94(\pm 0.02)\text{Å}$ indicate that there are two bidentate carbonate ions in the coordination sphere, while two oxygen backscatterers at $3.50(\pm 0.04)\text{Å}$ can be related to two monodentately bound carbonate groups. This structural environment, together with two calcium backscatterers at $3.95(\pm 0.03)\text{Å}$, is conclusively interpreted as neptunyl adsorbing at the calcite (104) face as an bidentate inner-sphere biscarbonato complex. Formation of this sorption complex at the calcite surface constitutes an important retention mechanism for neptunyl. No spectroscopic evidence for slow sequestration reactions like structural incorporation by subsequent dissolution and reprecipitation and was found within the 3 month reaction period.

Adsorption samples were prepared as described before [1]. As calcite we used Merck calcium carbonate suprapur with a BET surface of $1.3\text{ m}^2/\text{g}$. Suspensions were in equilibrium with calcite and air. The initial neptunyl concentration was $40\text{ }\mu\text{M}$, solution pH was 8.2. Two samples (Np-O1 and Np-O2) were allowed to react for three month, and two samples (Np-Y1 and Np-Y2) for 48 hours. After the reaction time suspensions were allowed to sediment and the supernatant was removed. The reacted calcite powder was filled as a wet paste into the SH01B-cryoholder, designed by the ROBL staff for low temperature EXAFS measurements of low activity radioactive samples. After sealing the sample holders the samples were frozen in liquid nitrogen

in order to stop the reaction. During the transport to the ESRF in Grenoble samples were cooled in dry ice. EXAFS measurements at the Np L3-edge (17610 eV) were performed at the Rossendorf beamline (ROBL) at the ESRF in fluorescence mode at low temperature (15 K) in a Helium cryostat in a glovebox. Parallel measurement of a zirconium foil (Zr K-edge: 17998 eV) in transmission mode enabled energy calibration of the spectra. We measured 15 spectra of sample Np-O2 and 16 spectra of sample Np-Y1. As we found no significant difference between the young (Np-Y1) and the old sample (Np-O2) we decided to analyze the structure from the spectrum with the better signal to noise ratio, which was the one measured from the old sample, Np-O2. The extracted EXAFS signal was used in a k-range from 2.0 \AA^{-1} to 10.2 \AA^{-1} . Using a larger k-range caused the noise in the spectrum to contribute significantly to the R-space spectrum. Hanning windows are used in the Fourier Transformations. The axial oxygen path was used to correct for phase shift. R-range was 1.0 \AA to 5.0 \AA , fitting was performed in R-space, and k-weights for fitting were 1, 2, and 3. Bond-valence calculations are used to check the plausibility of the of the obtained coordination environment of the central neptunium atom.

Results and Discussion

The goal of measuring EXAFS spectra of samples after different reaction times (48 h and three months) was to see if we can find spectroscopic evidence for recrystallization processes that lead to neptunyl incorporation into the calcite surface layers under calcite equilibrium conditions over extended reaction times. Indication for such processes was found in experiments on adsorption kinetics and in desorption experiments. However, no significant difference in the EXAFS spectra of samples Np-Y1 and Np-O2 could be observed.

Due to the better quality of the spectrum from sample Np-O2 we decided to use this spectrum for detailed analyses of the adsorption complex structure. The k^3 -weighted extracted EXAFS signal together with the model spectrum of sample Np-O2 is shown in Figure 1. Figure 2 displays magnitude and imaginary part of the corresponding Fourier transform spectra in R-space. A structural model giving a good fit between measured and modelled spectrum and saturating the bond-valence of the neptunium atom could be achieved using 5 different electron backscattering paths. Structural parameters obtained from the EXAFS data analyses are listed in table 1.

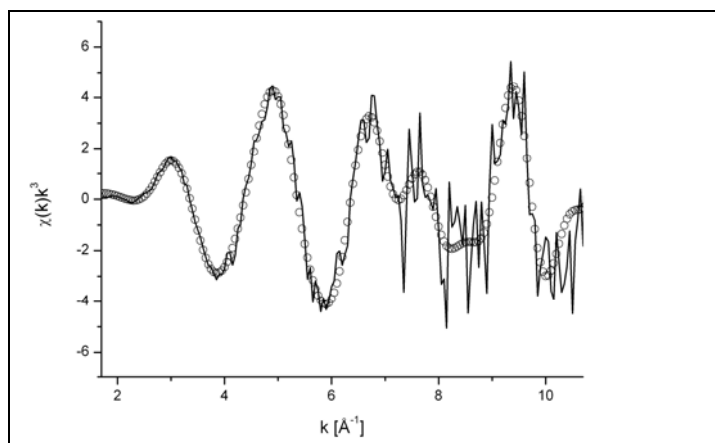


Figure 1: k^3 -weighted extracted EXAFS data (line) and model spectrum (circles) of sample Np-O2.

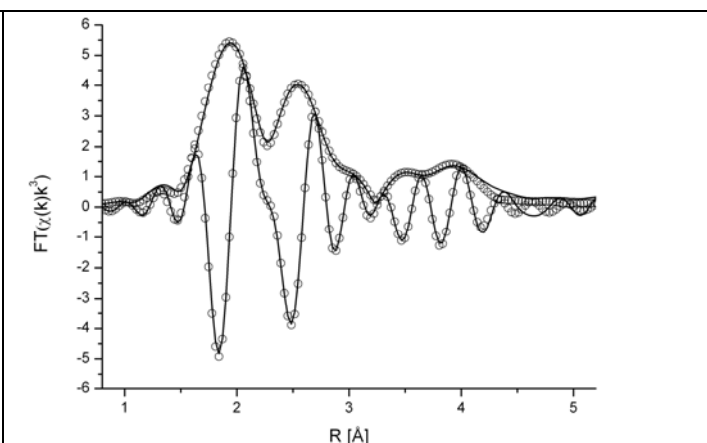


Figure 2: Fourier transform amplitude and imaginary part of the k^3 -weighted EXAFS data (line) and model spectrum (circles). Spectra are corrected for phase shift.

Table 1: Coordination numbers, N, distances, R (\AA), and Debye-Waller factors, σ^2 (\AA^2), resulting from EXAFS data analyses.

Backscatterer	N	R (\AA)	σ^2 (\AA^2)
O (O-ax)	2.0(± 0.1)	1.87(± 0.01)	0.001(± 0.001)
O (O-eq)	6.1(± 0.5)	2.51(± 0.01)	0.009(± 0.003)

C (C-bi)	2.7(\pm 1.2)	2.94(\pm 0.02)	0.001(\pm 0.003)
O (O-surf)	2.0(\pm 0.8)	3.50(\pm 0.04)	0.001(\pm 0.006)
Ca	1.8(\pm 1.0)	3.95(\pm 0.03)	0.003(\pm 0.004)

Uncertainties, in brackets, are twice the standard deviation calculated by the Artemis software. The amplitude reduction factor was fixed at $S_0^2 = 0.8$, relative shift in ionization energy $\Delta E_0 = 8(1)$ eV, and the goodness of fit parameter for all three k-weights together, $r = 0.007$. Number of independent points, $NI = 20$, 16 parameters were used to fit the data.

It is however not trivial to find a structural explanation for the measured model parameters. The $2.0(\pm 0.1)$ oxygen backscatterers at $1.87(\pm 0.01)$ Å can surely be related to the axial oxygen atoms (O-ax) of the linear neptunyl molecule. $6.1(\pm 0.5)$ oxygen backscatterers at $2.51(\pm 0.01)$ Å are addressed to the equatorial oxygen shell (O-eq). This coordination environment is in good agreement with bond-valence calculations. Using bond-valence parameters $R_0 = 2.035$ and $b = 0.422$, the bond valence sum (BV) for the central neptunium atom is: $BV = 4.94$.

The sorption site that results in the best agreement with measured bond distances and the coordination numbers can be found at step edges on the calcite (104) face. This leads us to the conclusion that the most probable sorption site for neptunyl at the calcite (104) face is at step edges, where neptunyl forms a bidentate inner sphere sorption complex with two monodentate coordinating carbonate groups from the calcite surface. On the solution side of the neptunyl ion two bidentate bound carbonate ions can be found. A ball-and-stick representation of this most likely sorption complex is shown in Figure 3.

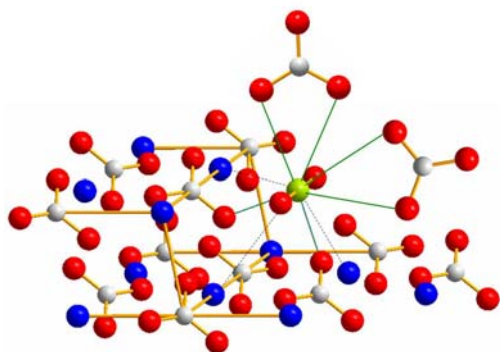


Figure 3: Structure of the most likely neptunyl-calcite adsorption complex according to the results of the EXAFS data analyses, bond-valence calculations, and geometrical considerations: neptunyl sorbs at step edges on the calcite (104) face as a bidentate inner-sphere bicarbonato complex. Indicated with green lines are the bonds to the six equatorial oxygen atoms. Dashed lines indicate the nearest calcium neighbours. (Np – green, Ca – blue, O – red, C – grey)

References

1. Heberling, F., Brendebach, B., Bosbach, D., Neptunium(V) adsorption to calcite, *J. Contam. Hydrol.* 102, pp. 246-252, **2008**