



	<b>Experiment title:</b> XAS investigation of adsorbed Np(V) onto ZrO <sub>2</sub>	<b>Experiment number:</b> 20-01-820
<b>Beamline:</b> BM20	<b>Date of experiment:</b> from: 2 <sup>nd</sup> July 2021 to: 8 <sup>th</sup> July 2021	<b>Date of report:</b> 23.11.2021
<b>Shifts:</b> 12	<b>Local contact(s):</b> André Rossberg and Andreas Scheinost	<i>Received at ESRF:</i>
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## Report:

The interactions of long-lived minor actinides such as neptunium (Np) with corroded phases in the near-field of a repository need to be considered in a safety assessment. Zirconia (ZrO<sub>2</sub>), the main corrosion product of the zircaloy cladding material of spent nuclear fuel rods, represents a first barrier for possible interactions with Np(V) – the most stable oxidation state of neptunium under oxidizing conditions.<sup>[1,2]</sup>

In this measurement campaign different Np(V)-ZrO<sub>2</sub> wet paste samples were investigated to gain a better understanding of the structure of the occurring Np(V) surface complexes and the oxidation state of neptunium. The samples were prepared under differing conditions (pH, [Np(V)], ionic strength), to study the speciation of Np(V) on the zirconia surface.

The samples were measured at the Rossendorf Beamline (ROBL-II) at ESRF using X-ray absorption spectroscopy (XAS). A closed-cycle He cryostat was used to cool the samples to 15 K during the measurement and the Np L<sub>3</sub>-edge spectra were recorded in fluorescence mode. Overall 12 samples were measured.

In a first step, we had to test the feasibility of XAS measurements on this system. The energy of the Zr K-edge (17,998 eV) is close to the energy of the commonly used Np L<sub>3</sub>-edge (17,610 eV), resulting in an interference of Zr in the measured Np L<sub>3</sub>-edge spectra. Thus, the Np EXAFS spectra could only be analyzed in a  $k$ -range up to  $k = 8.7 \text{ \AA}^{-1}$ . The approach to use the Np L<sub>2</sub>-edge with an energy (21,600 eV) above the Zr K-edge was not successful due to the intense signals of the Zr matrix overlapping the Np signal.

The XANES spectra showed that Np is still present as Np(V), thus no change in the oxidation state occurred during the surface interaction (spectra not shown). The obtained EXAFS spectra were utilized to gain information about the molecular environment of the Np(V) sorbed onto the ZrO<sub>2</sub> surface. Due to the interfering Zr signal, resulting in a shorter analyzable  $k$ -range (up to  $k = 8.7 \text{ \AA}^{-1}$ ), background subtraction problems occurred which impede the data analysis. Thus, the following results are preliminary. However, the influence of the background subtraction problem was very small on the Zr contribution of the EXAFS spectra. Since similar spectra were obtained for most of the 12 measured samples, all spectra were averaged due to statistic reasons.

This allows a first interpretation of the Np-Zr bonding situation. In Fig. 1 the average EXAFS spectrum and the fit with and without zirconium as a backscatterer are shown. A reasonable fit of the spectra was only acquired when Zr is included. Furthermore, the shell fit (Tab. 1) revealed a very short Np-Zr distance of 3.2 Å. This indicates the presence of inner-sphere bidentate Np(V) surface complexes, since longer Np-Zr distances are expected for a monodentate surface species. These preliminary results are in good agreement with literature data about Np(V) complexes on other mineral surfaces. IR studies showed the formation of Np(V) bidentate surface complexes on TiO<sub>2</sub><sup>[3]</sup> and EXAFS investigations revealed the formation of bidentate edge-sharing Np(V) complexes on corundum<sup>[4]</sup> and hematite<sup>[5]</sup>. At this point, no certain statement regarding the number of surface species can be made.

Until today, no work has been published showing EXAFS results of Np(V) surface complexes on zirconia. The gained structural information of the Np(V)-ZrO<sub>2</sub> surface species will contribute to a better understanding of the occurring molecular surface processes. Also the surface complexation thermodynamic constants that will be derived by using this knowledge will provide valuable information for a safety assesment of a repository. Further investigations are planned on the Np(V)-ZrO<sub>2</sub> system to study the influence of common inorganic ligands (e.g. PO<sub>4</sub><sup>3-</sup>) on the surface speciation.

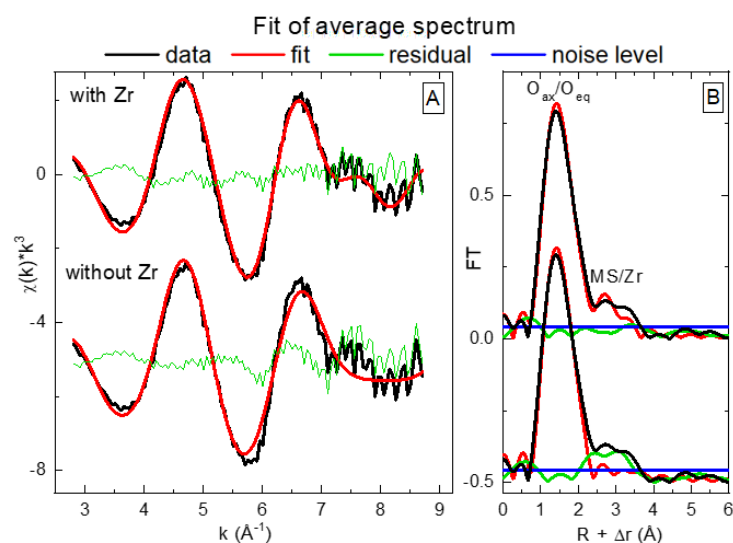


Fig. 1 A)  $k^3$ -weighted average EXAFS spectrum of all measured samples using the Np  $L_3$  absorption edge fitted with and without Zr as backscatterer and B) corresponding Fourier transformed EXAFS spectra.  $O_{ax}/O_{eq}$  are axial and equatorial oxygens, MS = multiscattering path Np- $O_{ax(1)}$ -Np- $O_{ax(2)}$ .

Tab. 1 Preliminary structural parameters derived from the  $k^3$ -weighed averaged EXAFS spectrum including Zr as backscatterer. Estimated standard deviations of the variable parameter as given from EXAFSPAK in parenthesis.

path / sample	CN	r / Å	$\sigma^2$ / Å <sup>2</sup>	$\Delta E_0$ / eV
Np- $O_{ax}$	2 <sup>f</sup>	1.827(5)	0.0032(5)	-3.4(8)
Np- $O_{eq}$	5 <sup>f</sup>	2.386(8)	0.0070(6)	-3.4(8)/
Np-Zr	1.7(9)	3.18(1)	0.009(5)	-3.4(8)/

<sup>f</sup> – fixed, /-linked parameter CN – coordination number  
r – radial distance  $\sigma^2$  – Debye-Waller factor  
 $\Delta E_0$  - shift in energy threshold

Multiscattering path (MS) Np- $O_{ax(1)}$ -Np- $O_{ax(2)}$  included.

## References

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