



ROBL-CRG

Experiment title:

EXAFS study of Np(VII) solutions

Experiment number:

20_01_029

Beamline:

BM 20

Date of experiment:

on: 29/09/2000

Date of report:

21/03/2001

Shifts:

3

Local contact(s):

Dr. Reich, Tobias

Received at ROBL:

27/03/2001

Names and affiliations of applicants (* indicates experimentalists):

Henry Moll*, Tobias Reich*, Christoph Hennig*, Harald Funke*, Susanne Pompe*, Katja Schmeide*, Andre Roßberg*, T.Ye. Zayarnaya*^{a)} and Thomas Fanghänel

Institute of Radiochemistry, Forschungszentrum Rossendorf e.V., P.O. Box 510119,
D-01314 Dresden, Germany

a) Institute of Metal Physics, Russ. Academy Sci., Ekaterinburg, Russia

Report:

Experimental. For synthesis of Np(VII), we followed in general the description given by Clark et al. [1]. Finally, ozone was bubbled through a mixture of $\text{NpO}_2(\text{OH})_2$ and 2.5 M NaOH. The solid dissolved to dark green Np(VII). The characteristic absorption maxima at 412 nm and 618 nm, and the molar absorption coefficients published in [2] were used to determine the Np(VII) concentration, 0.015 M, of the solution measured at ROBL. The absorption spectra of the solution measured before and after the XAS measurement showed no difference. The alkaline Np(VII) solution was hermetically sealed under O_3 atmosphere in a polyethylene cuvette of 3 mm diameter. The EXAFS transmission spectra were recorded at room temperature using a water-cooled Si(111) double-crystal monochromator of fixed-exit type ($E = 5\text{--}35$ keV) at the Rossendorf Beamline (ROBL) at ESRF, Grenoble. The energy scale was calibrated using the first inflection point of the absorption spectrum of a Y foil (17038 eV). The scattering phases and amplitudes were calculated for a cluster of $\text{NpO}_4(\text{OH})_2$ using FEFF7. The atomic coordinates were taken from $\text{Co}(\text{NH}_3)_6\text{NpO}_4(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ reported in [3].

Results and Discussion. The XANES spectrum of Np(VII) in alkaline solution is significantly different compared to those of Np(IV), Np(V), and Np(VI) [4]. The Np(VII) species shows different symmetry properties indicating that no actinyl unit is present as in Np(V) and Np(VI). Soderholm et al. [5] reported a similar XANES spectrum of their Np(VII) sample. Four oxygen atoms at 1.89 Å are coordinated in the first shell around Np (Tab. 1 and Fig. 1). The Debye-Waller factor of 0.0020 \AA^2 is typical for actinyl compounds indicating a short and strong bond. The distance of these oxygens is significantly longer compared to Np(V), 1.82 Å, and Np(VI), 1.75 Å [4]. The amplitude of this shell is larger compared to “normal” actinyl compounds [4].

Table 1. EXAFS structural parameters measured for dark-green Np(VII) in 2.5 M NaOH. In parenthesis XRD values are given that were taken from reference [3].

Sample	Shell	N	σ^2 (\AA^2)	R (\AA)	ΔE_0 (eV)
0.015M Np(VII) in 2.5M NaOH	Np=O	3.6 ± 0.3 (4.0)	0.0020	1.89_4 (1.88 ₆)	-5.0
	Np-O	3.3 ± 1.3 (2.0)	0.0133	2.32_6 (2.32 ₃)	

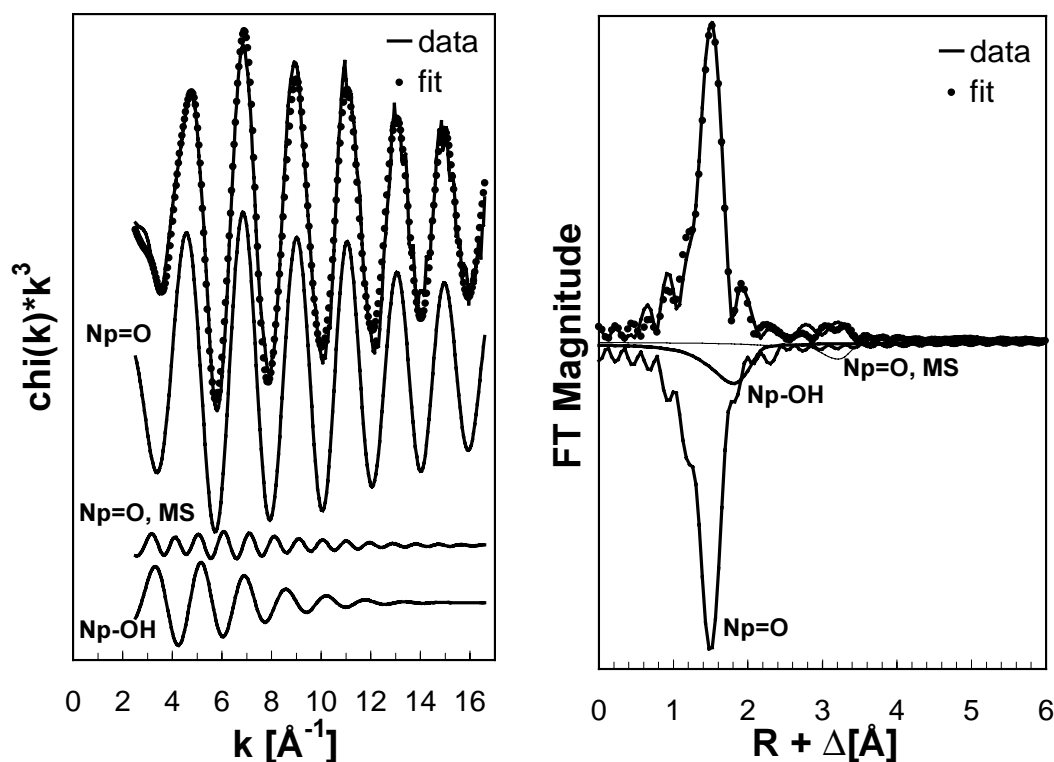


Fig. 1. Np L_{III} -edge k^3 -weighted EXAFS data including the best fit and corresponding FT measured for 0.015 M Np(VII) in 2.5 M NaOH.

An average coordination number of 3 and a distance of 2.33 \AA were determined for the second shell. The error of N is large because of the low amplitude and the strong interference with the “yl” oxygens. The atomic surrounding of Np(VII) in solution measured by EXAFS is in excellent agreement with the XRD results (see Tab. 1) of $\text{Co}(\text{NH}_3)_6\text{NpO}_4(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ [3]. To summarize, the XAS experiments and additional information from XRD lead to the conclusion that the structure of Np(VII) in alkaline solution is most likely $\text{NpO}_4(\text{OH})_2^{3-}$.

We will compare our experimental findings with new quantum chemical calculations.

References

- [1] Clark, D. L., et al., *J. Am. Chem. Soc.* **119**, 5259 (1997).
- [2] Spitsyn, V.I., et al., *J. Inorg. Nucl. Chem.* **31**, 2733 (1969).
- [3] Grigorev, M.S., et al., *Radiokhimija* **28**, 690 (1986).
- [4] Reich, T., et al., *Radiochim. Acta* **88**, 633 (2000).
- [5] Soderholm, L., et al., in press (2000).