ROBL-CRG	**Experiment title:** First EXAFS Measurement of Neptunium Solutions at ROBL	**Experiment number**: 20_01_02
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Report:

Experimental

Two series of aqueous solutions containing 50 and 5 mMol/L neptunium in three different oxidation states were prepared for EXAFS measurements at the new Rossendorf Beamline (ROBL) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. Solution 1 consisted of 50 mMol/L Np(IV) in 0.1 M HNO_3 and 2 M H_2SO_4. The composition of solutions 2 and 3 was 50 mMol/L Np(V) and Np(VI), respectively, in 0.1 M HNO_3. Solutions 4 – 6 were identical to solutions 1 – 3 except for the lower Np concentration of 5 mMol/L. The starting material for the sample preparation was solid $NpO_2(NO_3)$ (AEA Technology, QSA GmbH). It was dissolved in 0.1 M HNO_3. The different oxidation states of Np were obtained by electrochemical oxidation/reduction in a conventional H-formed electrolysis cell with a diaphragm between anode and cathode. The oxidation state of neptunium and its stability with time were determined for the 5 mMol/L Np solutions by UV-Vis spectroscopy using the characteristic absorption bands of Np(IV), Np(V), and Np(VI) at 967 nm, 980 nm, and 1223 nm, respectively /1/.

For the measurements, 4 ml of the solution were filled in a polyethylene cuvette, which was sealed and put in a polyethylene bag. Multiple scans of the Np L_{III}-edge EXAFS of solutions 1 – 6 were collected in transmission mode at room temperature at ROBL using the Si(111) double-crystal monochromator in fixed-exit mode. The energy scale was calibrated using the first inflection point of the absorption spectrum of a Zr foil (17998 eV). The scattering phases and amplitudes where calculated for hypothetical clusters of NpO_8S_2, NpO_2O_4, and NpO_2O_5 using FEFF6.

Results

The raw EXAFS data and the best theoretical fit for solutions 1 – 3 are shown in Fig. 1. The obtained structural parameters are given in Tab. 1. In solution 1 Np(IV) is surrounded by 11

oxygen atoms at a distance of 2.39 Å. In the second coordination sphere we observed two sulfur atoms with a Np-S distance of 3.07 Å. This distance corresponds to a bidentate coordination of the SO_4^{2-} ion to the Np. Using the Np-O distance of 2.39 Å and the structural parameters of the SO_4^{2-} unit (S-O = 1.51 Å, angle O-S-O = 109° /2/), the calculated Np-S distance of 2.93 Å is in good agreement with the measured value.
Both Np(V) and Np(VI) solutions 2 and 3 show the structural parameters of the actinyl ion. In case of Np(V), the distance to the axial oxygen atoms, O_{ax}, is 1.82 Å. In the equatorial plane the Np is surrounded by 4 water molecules with a Np-O_{eq} distance of 2.49 Å. The increase of the Np oxidation state from Np(V) to Np(VI) leads to a shortening of the axial and equatorial oxygen bonds by 0.07 Å and an increase of the number of water molecules attached to the neptunyl from four to five. The bond distances Np-O_{ax} and Np-O_{eq} of the Np(VI) solution are 1.75 Å and 2.42 Å, respectively.
The analysis of the 5 mMol/L Np solutions 4 – 6 gave results (not shown here) similar to the 50 mMol/L solutions. There is only a small increase of the coordination number of sulfur from 2.2 to 2.8 when going from 50 mMol/L to 5 mMol/L Np(IV).
The observed structural parameters for the Np-O bond distances of Np(IV) and Np(V) are in good agreement with the values reported for 5 mMol/L Np in chlorine solution /3/. The structural parameters for Np(IV) sulfate and Np(VI) hydrate given in Tab. 1 are reported for the first time.

References

/1/ Keller, C., The Chemistry of the Transuranium Elements, Verlag Chemie, Weinheim, 1971, p. 294
/2/ Hollemann, A.F., Lehrbuch der anorganischen Chemie, 101th Ed., Walter de Gruyter 1995, p. 585.
/3/ Allen, P.G., et al, Inorg. Chem. **36** (1997) 4676.

Tab. 1: EXAFS structural parameters for 50 mMol/L Np solutions.

Sample	Shell	R(Å)	N	$\sigma^{2\ a)}$
1, Np(IV)	Np-O	2.39	11.3(4)	1.18
	Np-S	3.07	2.2(3)	0.70
2 Np(V)	Np-O_{ax}	1.82	1.9	0.23
	Np-O_{eq}	2.49	3.6(2)	0.61
3 Np(VI)	Np-O_{ax}	1.75	2.0	0.15
	Np-O_{eq}	2.42	4.6(2)	0.56

a) σ^2 in units of 10^{-2} Å^2

Fig. 1: Raw Np L_{III}-edge k^3-weighted EXAFS spectra (left) and corresponding Fourier transforms (right) of 50 mMol/L Np solutions. Solid line – experiment; dots – theoretical fit.