ROBL-CRG	**Experiment title:** EXAFS Measurement of Pu Hydrates	**Experiment number:** 20-01-13
Beamline: BM 20	**Date of experiment:** from: 03.12.1999 to: 04.12.1999	**Date of report:** 11.03.2000 *Received at ROBL:* 11.03.2000
Shifts: 4	**Local contact(s):** T. Reich	
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Report:

Experimental

Plutonium(VI) hydrate was prepared by dissolution of PuO_2 (Pu-242, AEA Technology, QSA GmbH) and electrochemical oxidation. Part of this solution was reduced to Pu(III) in an electrochemical cell. The Pu(III) and Pu(VI) hydrates were in perchloric and nitric media (1 M acidic solution), respectively. The final Pu concentration was 50 mol/L. The Pu oxidation states were confirmed by UV/Vis spectroscopy. For the measurements 4.7 mL of solution (7.5 MBq) was filled and sealed in polyethylene cuvettes. The samples were measured at the Rossendorf Beamline ROBL at the European Synchrotron Radiation Facility (ESRF), Grenoble, France within 48 hours after their preparation.

Multiple scans of the Pu L_{III}-edge EXAFS were collected in transmission mode at room temperature using the Si(111) double-crystal monochromator in fixed-exit mode /1/. 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 PuO_8, and PuO_2O_5 using FEFF6.

Results

As one can see from the XANES spectra given in Fig. 1, the L_{III} absorption edge of Pu(VI) is shifted by 4 eV toward higher energy as compared to that of Pu(III). The energy shift and the distinct XANES features of these two Pu hydrates can be used for the determination of the Pu oxidation states /2/. The different electronic and molecular structures of Pu(III) and Pu(VI) hydrates are also reflected in the EXAFS shown in Fig. 2. The coordination sphere of Pu(III) hydrate can be written as $Pu(H_2O)_8^{3+}$ with an average Pu-O bond distance of 2.48 Å. The Fourier transform corresponding to the EXAFS of Pu(VI) hydrate shows two coordination shells. The Pu(VI) forms a plutonyl ion $PuO_2(H_2O)_{4\text{-}5}^{2+}$. The axial and equatorial Pu-O bond distances are 1.74 and 2.42 Å, respectively. The structural parameters of Pu(VI) hydrate are nearly identical to those of U(VI) and Np(VI) hydrates (see Tab. 1), which were measured recently at ROBL /3/.

Reference

/1/ W. Matz et al., J. Synchrotron Rad., **6**, 1076 (1999)
/2/ S.D. Conradson et al., Polyhedron, **17**, 599 (1998)
/3/ T. Reich et al., Radiochim. Acta (accepted for publication).

Tab. 1: EXAFS structural parameters for 50 mMol/L Pu hydrates and comparison with 50 mMol/L Np(VI) and U(VI) hydrates.

Sample	Shell	R(Å)	N	$\sigma^{2\ a)}$
Pu(III)	Pu-O	2.48	7.6(2)	1.02
Pu(VI)	Pu -O_{ax}	1.74	1.9	0.12
	Pu -O_{eq}	2.42	4.4(2)	0.50
Np(VI)	Np-O_{ax}	1.75	2.0	0.15
	Np-O_{eq}	2.42	4.6(2)	0.56
U(VI)	U-O_{ax}	1.76	1.9	0.12
	U-O_{eq}	2.41	4.9(2)	0.61

a) σ^2 in units of 10^{-2} Å^2

Fig. 1: Pu L_{III}-edge XANES spectra Pu(III) and Pu(VI) hydrates.

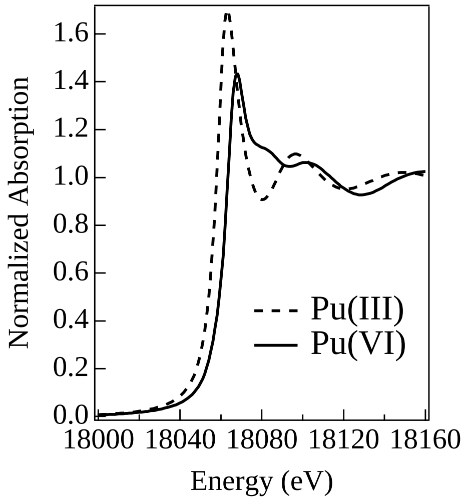
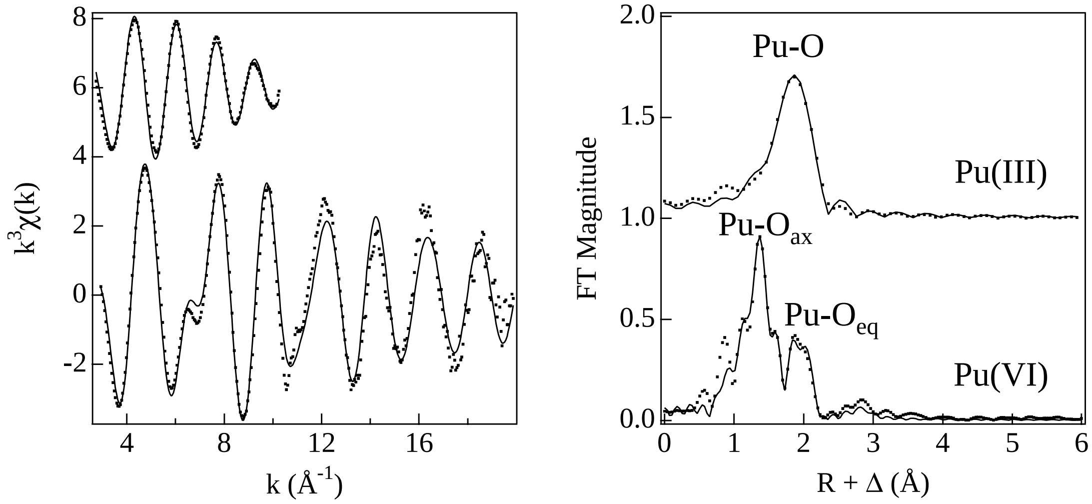


Fig. 2: Raw Pu L_{III}-edge k^3-weighted EXAFS spectra (left) and corresponding Fourier transforms (right) of 50 mMol/L Pu hydrates. Solid line – theoretical fit; dots – experiment.



8
6
4
2
0
-2
$k^3\chi(k)$
4
8
12
16
k (Å^{-1})
2.0
1.5
1.0
0.5
0.0
FT Magnitude
Pu-O
Pu(III)
Pu-O$_{ax}$
Pu-O$_{eq}$
Pu(VI)
0
1
2
3
4
5
6
R + Δ (Å)