



ROBL-CRG

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Report:

The near-neighbor surrounding of Pu(III,IV) sorbed onto humic substances and Bio-Rex70 was studied at pH 2 by XAFS spectroscopy. The results are compared with literature data of Pu(III) and Pu(IV) hydrates.

Experimental: A Pu(III) stock solution (^{242}Pu), prepared by electrochemical reduction of a Pu(VI) solution, was used to prepare Pu(III) samples from synthetic humic acid type M42, Kranichsee fulvic acid (KFA), and Bio-Rex70 (from Bio-Rad) at pH 2 under inert gas conditions. The Pu loading of the resulting wet pastes of M42, KFA and Bio-Rex70 was 61, 71 and 6 mg Pu per g sorbent, respectively. Pu L_{III} -edge XAFS spectra were collected in fluorescence mode at the Rossendorf Beamline at the ESRF in Grenoble.

Results: The trivalent oxidation state of Pu in the stock solution as well as in the supernatants obtained during preparation of the Pu sorbates was verified by UV-vis absorption spectroscopy using the absorption band at 600 nm. Pu(IV) could not be detected (at 470 nm) in the solutions stored under inert gas conditions, even 4 months after sample preparation. That means, an oxidation of Pu(III) by humic substances or Bio-Rex70 can be excluded. However, according to the XANES spectra of the Pu sorbates the samples contain predominantly Pu(IV) with small amounts of Pu(III). That means, the trivalent oxidation state of Pu was not stable within the time of our experiment. The most likely reason is that during the sample transport to the beamline oxygen diffused through the PE bags and the Capton tape used for sealing the Teflon sample holders for pastes.

The EXAFS oscillations and the Fourier transforms of M42 and KFA, shown in Fig. 1, are similar to each other but different from those of Bio-Rex70. The structural parameters are given in Tab. 1.

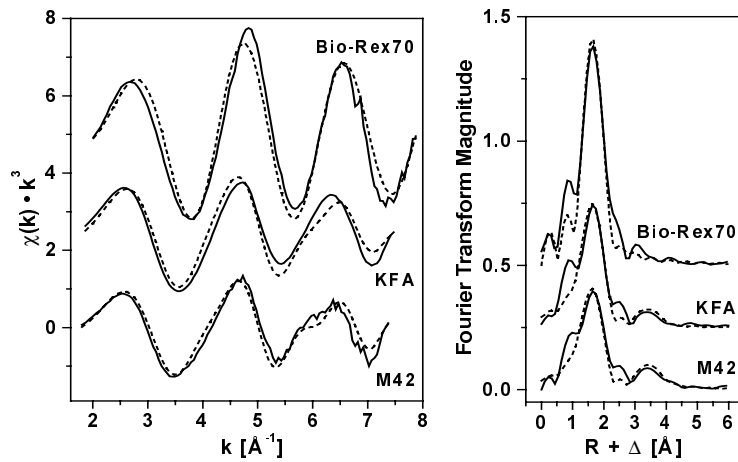


Fig. 1: Raw Pu L_{III}-edge k^3 -weighted EXAFS spectra of Pu samples and corresponding Fourier transforms (without phase corrections). Solid lines: experiment, dashed lines: fit.

Tab. 1: Structural parameters of Pu samples

Sample	Shell	N	R [Å]	$\sigma^2[\text{Å}^2]$
Pu-M42	Pu-O	7.8 ± 1.7	2.38 ± 0.03	0.0250
	Pu-Pu	1.9 ± 1.9	3.78 ± 0.04	0.0086
Pu-KFA	Pu-O	8.3 ± 1.8	2.38 ± 0.03	0.0228
	Pu-Pu	1.5 ± 2.4	3.77 ± 0.05	0.0112
Pu-Bio-Rex70	Pu-O	6.8 ± 1.2	2.34 ± 0.01	0.0098
Pu(III)·nH ₂ O /1/	Pu-O	7.6 ± 0.6	2.48 ± 0.01	0.0102
Pu(IV)·nH ₂ O /2/	Pu-O	8	2.39	0.0118

The 95 % confidence limits are given for N and R as estimated by EXAFSPAK.

Within the experimental error, the coordination number of the Pu-O shell of all samples is comparable with those of Pu(III) and Pu(IV) hydrates. The bond length of the Pu-Bio-Rex70 sorbate, which contains the highest amount of Pu(IV), is about 0.05 Å shorter than that of Pu(IV) hydrate. A similar shortening (0.04 Å) was found for Np(IV) samples due to complexation by humic substances and Bio-Rex70 /3/.

According to the XANES results, the Pu sorbates of M42 and KFA contain a slightly higher amount of Pu(III) compared to the Pu-Bio-Rex70 sorbate. This results in a slightly larger bond length ($R_{\text{Pu-O}} = 2.38$ Å) which is due to the larger ionic radius of Pu³⁺ (1.12 ± 0.02 Å) compared to Pu⁴⁺ (1.01 ± 0.02 Å) /4/. The broader distribution of R of the humates due to the two oxidation states is evident in the larger Debye-Waller factor.

The Fourier transforms of the M42 and KFA samples (cf. Fig. 1) show an additional broad peak at about 3.4 Å. Fitting a Pu-Pu shell, 1 to 2 Pu atoms were found at a bond distance of 3.78 Å. This indicates the formation of polynuclear Pu species which is characteristic for Pu(IV). This effect was not observed for Pu-Bio-Rex70, probably due to the lower Pu loading of Bio-Rex70 compared to the humic substances.

The results have shown that in case of humate and Bio-Rex70 sorbates of such redox sensitive actinide ions as Pu much attention has to be paid to the selection of sample containers to minimize diffusion of oxygen. Another possibility is to prepare the samples on-site directly before the XAFS measurements.

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References: /1/ Reich, T., et al., Report FZR-285, 72 (2000); /2/ Ankudinov, A.L., et al., Phys. Rev. B 57, 7518 (1998); /3/ Schmeide, K., et al., Proceedings of Internat. Conf. Actinide-XAS-2000, Grenoble, France, in press; /4/ Neck, V., Kim, J.I., Radiochim. Acta 88, 815 (2000).