



	Experiment title: EXAFS and XANES investigation of plutonium sorption complexes on iron minerals	Experiment number: 20-01-693
Beamline: BM20	Date of experiment: from: 22/07/2009 to: 25/07/2009 07/07/2010 to: 12/07/2010	Date of report: 3 rd February 2011
Shifts: 9+15	Local contact(s): Andreas C. Scheinost	<i>Received at ESRF:</i>
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Report:

Due to their redox reactivity, surface sorption characteristics, and ubiquity as corrosion products or natural sediment constituents, iron(II)-bearing minerals control to a large extent the environmental fate of actinides. In this experiment, Pu-L_{III}-edge XANES and EXAFS spectra were collected of a total of 22 samples, consisting of ²⁴²Pu(III) or ²⁴²Pu(V) reacted under anoxic conditions for 40 days or 6 months with magnetite, mackinawite, siderite, hematite, maghemite, or goethite. In the presence of the iron(III)-minerals hematite, goethite and maghemite, Pu(V) was largely reduced to Pu(IV) (30 % Pu(V), 70% Pu(IV) after 6 months reaction with hematite at pH8, 80% Pu(IV) after 6 months reaction with maghemite, pH6). In magnetite suspensions, reduction of Pu(V) to Pu(III) and formation of a Pu(III)-magnetite surface sorption complex was observed (see below for details). At the two pH value (pH 6 and pH8) tested for mackinawite suspensions and for a reaction period of 6 months, both aqueous Pu(V) and Pu(III) transformed into PuO₂. Small differences between EXAFS spectra as a function of initial Pu oxidation state and reaction pH are apparent and currently being interpreted. PuO₂-Pu(III) mixtures result from addition of Pu(V) or Pu(III) to siderite suspensions (e.g. 67% PuO₂, 33 % Pu(III) after reaction of initially Pu(V) with siderite for 40 d). So far, it is not clear to what extent the oxidation state composition of the reaction product depends on reaction time and initial Pu oxidation state and in how far other parameters such as variations in reaction pH and associated variations in Fe(II) concentrations and redox potential are crucial.

These results highlight the necessity to consider under anoxic conditions Pu(III) species in addition to PuO₂ for risk assessment. Our results also demonstrate the necessity to combine thermodynamic calculations and spectroscopic data.

Results highlight:

The three Pu-magnetite spectra in Figure 1, obtained by reaction of Pu(III) or Pu(V) with magnetite at pH6 or pH8 for 40 days, are characterized by very similar edge and peak positions, irrespective of the initial Pu oxidation state and the reaction pH and strongly resemble the (Pu^{III})_{aq} spectrum in position and shape. Using an Iterative Target Test (ITT) (1) on the XANES and EXAFS regions of the spectra, Pu(III) contents higher than 90 % were found for all three. Also shell fitting of the first peak in the Fourier Transform yields Pu-O distances of 2.48 Å to 2.49 Å, characteristic of aqueous Pu(III) complexes. Under the given experimental conditions, the oxidation state of Pu after reaction with magnetite appears therefore to be independent of the initial oxidation state (III or V) suggesting that thermodynamic equilibrium has been attained. To elucidate the structure of the Pu(III) species on magnetite, shell fitting was extended to the FT peaks beyond the

oxygen coordination sphere. A second shell could be fitted with backscattering from three to five Fe atoms at a distance of 3.54 Å, suggesting either a sorption complex or formation of a solid phase. The sorption complex hypothesis was tested using FEFF-Monte Carlo (MC) modeling (2) on the k^3 -weighted EXAFS spectrum of the Pu(V)-Magnetite-pH8 sample. One geometrically specific position in relation to magnetite, situated on a (111) surface with octahedral termination, was identified (Fig. 1d). In the corresponding surface complex, one Pu atom is linked via three oxygen atoms to three edge-sharing FeO_6 -octahedra. The contribution of Pu-Pu backscattering to the experimental spectrum could be ruled out, thereby excluding formation of a dimeric surface complex or PuIII(hydr)oxide clusters. The radial Pu-atom distances found in the "raw" structure of the sorption complex were refined by reverse Monte Carlo (RMC) simulation. The resulting $\chi(k) \times k^3$ spectrum and the experimental spectrum (Fig. 1b) are in excellent agreement. The refinement yields the Pu-O and Pu-Fe radial pair distribution functions (RPDF) (Fig. 1c), wherein the first Pu-O peak corresponds to 9 oxygen atoms at 2.49 Å and the first Pu-Fe peak to three iron atoms at 3.54 Å. Due to the tridentate nature of the complex, it is likely to be very stable and play an important role in controlling Pu-magnetite reactions and Pu mobility under anoxic conditions. Details on sample preparation and analysis methods can be found in (3).

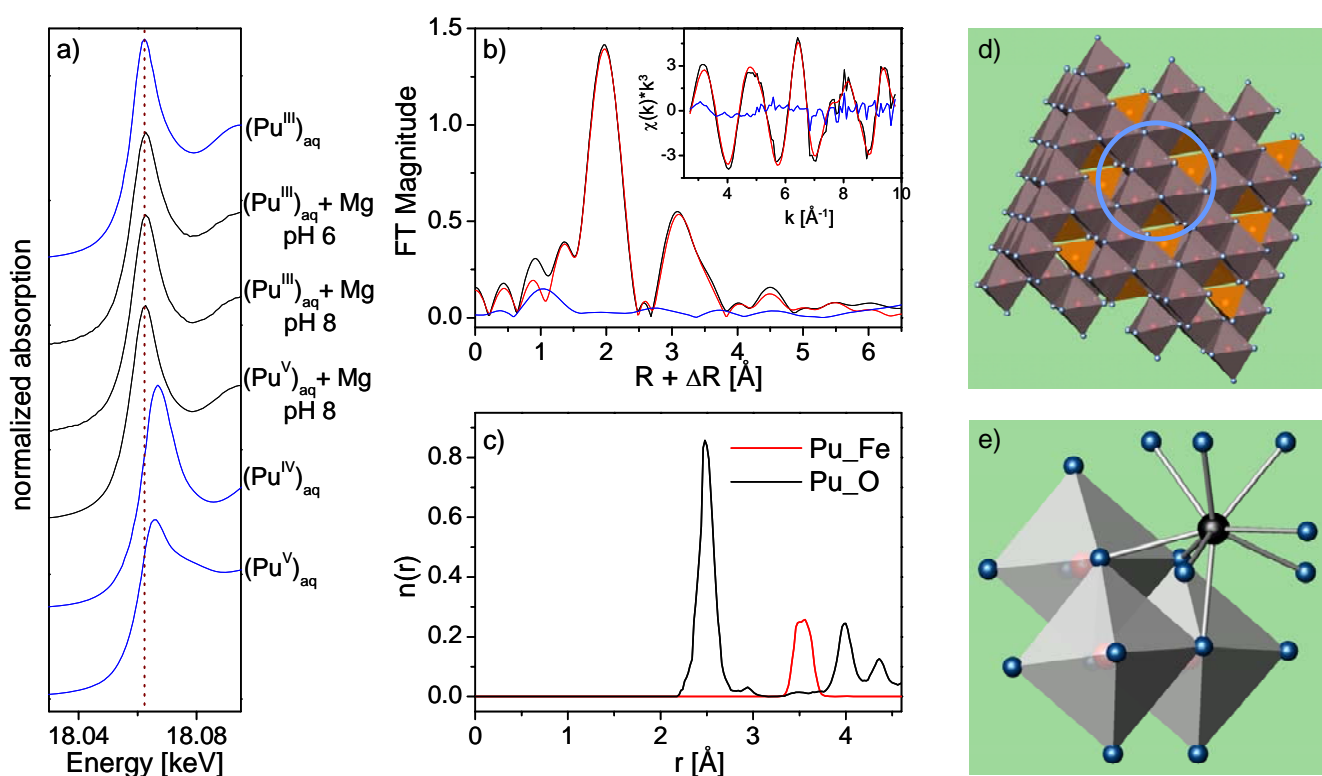


Figure 1. a) Experimental Pu-L_{III} XANES spectra of Pu reacted with magnetite (black) and $(\text{Pu}^{\text{III}})_{\text{aq}}$, $(\text{Pu}^{\text{IV}})_{\text{aq}}$ and $(\text{Pu}^{\text{V}})_{\text{aq}}$ for reference (blue); b) experimental Pu-L_{III} EXAFS spectrum of $(\text{Pu}^{\text{V}})_{\text{aq}} + \text{Mg}$, pH 8 sample and final spectrum resulting from radial refinement by MC simulation, FT and chi-spectrum (inset) (black - experimental, red - MC simulation, blue - residual); c) Pu-O and Pu-Fe radial pair distribution functions resulting from radial refinement. d) octahedrally terminated (111) face of magnetite with position of Pu(III) sorption circled e) sorption complex structure of Pu(III) on edge-sharing FeO_6 -octahedra (Pu – black, O – blue, Fe – red).

References:

- (1) Rossberg, A. et al. *Anal Bioanal Chem* **2003**, 376 (5), 631-638.
- (2) Rossberg, A. and Scheinost, A. C. *Anal Bioanal Chem* **2005**, 383 (1), 56-66.
- (3) Kirsch, R. et al., in prep. for Environ. Sci. Technol.