



Experiment title:
EXAFS and XANES investigation of plutonium sorption complexes on iron minerals

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Report:

Iron mineral-plutonium samples resulting from exposure of iron minerals to aqueous tri- and pentavalent plutonium under laboratory anoxic conditions (≤ 10 ppmv O₂) were analyzed using X-ray absorption spectroscopy (XAS) to monitor the time and mineral dependent *in-situ* oxidation state of Pu associated with the solid phase. Iron minerals used included mackinawite, chukanovite, magnetite, maghemite, hematite and goethite, thus covering a number of chemically and structurally different minerals that are relevant to the environmental fate of plutonium both in natural (soils and sediments) and engineered settings (e.g. nuclear waste repositories).

It was found that the oxidation state in which plutonium is present depends strongly on the structure and Fe(II) content of the solid. In particular, we found that the amount of Pu present in the trivalent oxidation state depends not only on the redox conditions but also on the available mineral surface area.

In summary, the XAS results can be outlined as follows:

With hematite and goethite, Pu associated with the solid phase is mainly in the tetravalent oxidation state, with some Pu possibly present as Pu(V). This result was independent of whether Pu(III) or Pu(V) had been added to hematite. Reduction of Pu(V) is most likely due to trace amounts of Fe(II) contained in hematite and goethite due to the synthesis route chosen and despite the fact they are Fe(III) (oxyhydr)oxides. For these minerals, the XAS spectra give no indication for the presence of PuO₂ but do not permit the identification of a surface complex either.

With magnetite (Fe₃O₄), in which ideally one third of the iron is present as Fe(II), reduction of Pu(V) to Pu(III) and stabilization of Pu(III) in the trivalent oxidation state is observed. From the EXAFS spectra in combination with Feff-Monte Carlo simulation, an inner-sphere surface complex formed by Pu(III) on magnetite (111) faces could be identified (Fig. 1). Presence of PuO₂ in addition to the Pu(III) surface complex in the sample with the highest Pu/mineral ratio and highest reaction pH suggest that once the aqueous Pu(III) concentration in equilibrium with the surface complex exceeds that in equilibrium with PuO₂ (PuO₂(am,hyd)), formation of a PuO₂ solid phase occurs as will be expected from thermodynamics.

With mackinawite (FeS) at the lowest reaction pH (pH 6), only Pu(III) was found associated to the solid phase, probably in the form of an outer-sphere sorption complex. At higher pH values (pH 7 - 8.5), PuO₂ formed and in two out of five samples small amounts of Pu(III) were also present, indicating that above pH 6

sorption of Pu(III) also occurs. With chukanovite ($\text{Fe}_2(\text{CO}_3)(\text{OH})_2$), 15 to 40 % of plutonium associated with the solid phase were present as Pu(III), the remaining 60 to 85 % being present as PuO_2 .

Our results indicate that the percentage of Pu that, in a given system, can be expected to be present as surface bound Pu(III) should be dependent on

- pe, pH, ionic strength and concentration of complexing ligands, as the concentration of Pu(III) in thermodynamic equilibrium with $\text{PuO}_2(\text{am,hyd})$ decreases with increasing pH and pe and changes with increasing ionic strength
- The crystallinity and particle size of PuO_2 , as at fixed pH conditions, $[\text{Pu(III)aq}]$ is expected to increase with decreasing particle size and increasing disorder in the PuO_2 structure
- The type of the mineral (oxide, sulfide, carbonate) and its surface area.
- Presence of other ions that can compete with Pu(III) for sorption sites.

Remeasuring sample over time (after 8 months and 2.5 years of aging) we found non-detectable or minor changes of oxidation state and structure for Pu reacted with hematite, magnetite and mackinawite. For Pu(V) and Pu(III) reacted with maghemite that contained traces of Fe(II), in contrast, a considerable change in oxidation state took place: From predominantly Pu(IV) both samples (where Pu had been added as Pu(V) or Pu(III)) evolved to about 60 % Pu(III), 40 % Pu(IV). As samples were aged in the dark, photo-reduction as driving force for this reduction of Pu(IV) to Pu(III) can be excluded. Most likely, Fe(II) was concentrated in the central part of maghemite particles and exchanged electrons with surface associated Pu and the surrounding solution only slowly. The measured redox potential in suspension also changed over this two year period from a pe value of 4 to 1.5. It thus appears that iron oxide associated Pu changes its oxidation state readily according to the redox milieu created by the mineral and the surrounding solution.

Results highlight:

Through application of Feff Monte Carlo simulation to XAS spectra of Pu(III) associated with magnetite, the structure of the Pu(III) sorption complex on magnetite (111) faces could be elucidated (Fig. 1). Due to its tridentate nature, this complex is likely to be very stable and play an important role in controlling plutonium solution concentrations and mobility under anoxic conditions in presence of magnetite (1).

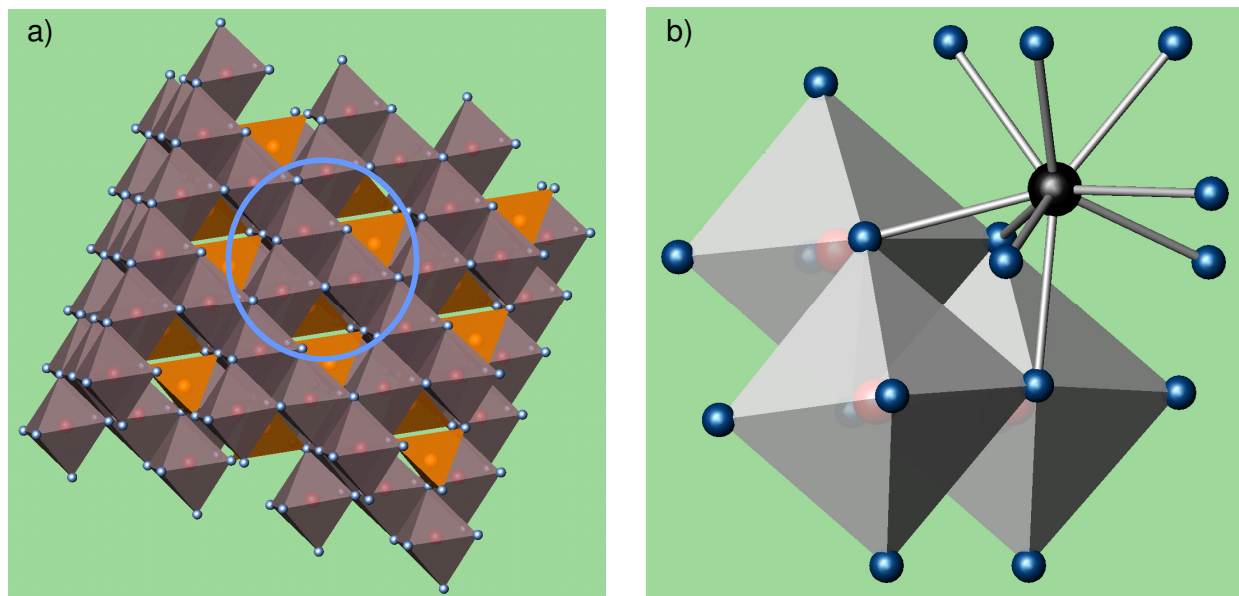


Figure 1. a) Octahedrally terminated (111) face of magnetite with position of Pu(III) sorption circled e) sorption complex structure of Pu(III) on edge-sharing FeO_6 -octahedra (Pu – black, O – blue, Fe – red).

References:

- (1) Kirsch, R. et al., Environ. Sci. Technol. 45 (2011) 7267-7274.