

## Newly recognized hosts for Uranium in the Hanford 300 Area vadose zone

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The U.S. Department of Energy's Hanford Site in Washington was the site of cold war plutonium production and its subsurface is extensively contaminated with uranium, as well as other toxic and radioactive metals and organic compounds. Several investigators have explored uranium contamination at the Hanford 300 Area using electron microprobe analysis and synchrotron-based x-ray methods [1-3]. We extend this work by investigating uranium hosts at two depths in sediments beneath the former North Process Ponds using electron microprobe analysis (EMPA) and transmission electron microscopy (TEM) of samples prepared with a focused ion beam (FIB) instrument.

We have identified 6 hosts for uranium in these samples using electron microprobe analysis. Consistent with previous studies, we find uranium hosted by a Cu-uranyl phosphate presumed to be metatorbernite  $[\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}]$  and clay coatings on sediment clasts. In addition, we find uranium associated with aluminosilicate vug linings in basalt clasts; weathered basaltic glass (palagonite); Mn-Fe oxides; and a Zr-rich material. Samples of each host have been prepared for transmission electron microscopy using a focused ion beam (FIB) instrument. Selected area electron diffraction (SAED) in the TEM unequivocally confirms the identity of metatorbernite. The aluminosilicate vug linings are poorly crystalline and the palagonite is amorphous. The Zr-rich material is amorphous and appears to be an oxide, although electron energy-loss spectroscopy (EELS) shows that it contains a significant amount of phosphorous (Zr:P atomic ratio ~ 5:1).

Although metatorbernite and clay minerals are clearly significant sinks for uranium at Hanford, our findings illustrate the importance of amorphous and poorly crystalline materials in the uptake of uranium, and further highlight the complexity of uranium behavior in the Hanford vadose zone.

[1] Arai *et al.* (2007) *ES&T* **41**, 4633-4639. [2] Catalano *et al.* (2006) *ES&T*. **40**, 2517-2524. [3] McKinley *et al.* (2007) *Vadose Zone J.* **6**, 1004-1017.

## Spectroscopic characterization and quantification of M(III)/clay mineral outer-sphere complexes

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The behavior of radionuclides in the environment is determined by interface reactions like adsorption, ion exchange and incorporation processes. Therefore, interaction mechanisms and processes need to be understood on a molecular level. This can only be achieved by application of spectroscopic methods.

Because of the reductive conditions in the environment of a waste repository in deep geologic formations heavy metal ions are present in low oxidation states. Both, Am and Cm contribute significantly to the radiotoxic inventory of high level nuclear waste and are present as trivalent species under repository conditions. Depending on redox conditions and pH, plutonium can also exist predominantly in the trivalent state. Cm(III) was chosen as a representative of the trivalent actinides because its fluorescence spectroscopic sensitivity allows sorbed species to be studied on a molecular level at nano-molar concentrations. TRLFS has been proven to be a versatile tool for Cm(III) speciation studies and for sorption studies on various solids. It is capable of identifying different species as well as determining their hydration status, thus allowing inner-sphere surface complexes and species incorporated in the crystal lattice of the solids, to be distinguished from each other.

The relevance of clay minerals for designing a nuclear waste repository is high. On the one hand clay formations are in discussion as appropriate host rock on the other hand one considers the use of clay minerals as backfill material in various waste repository concepts. Furthermore clay minerals are omnipresent solid phases in the ecosphere. Clay minerals are well known as strong sorbents for radionuclides. Notably, smectites exhibit high cation exchange capacities and cation exchange reactions dominate cation-clay interaction under certain geochemical conditions (low pH, low ionic strength). Trivalent actinide cations keep their hydration sphere upon sorption in this case and display fluorescence spectra similar to those of non-sorbed aquo ions. Up to now, there is no direct method available to quantify those outer-sphere bound cations and to differentiate them from non-sorbed aquo ions. Here, we present a method based on TRLFS measurements, to directly quantify outer-sphere bound Cm(III) by the quenching effect exerted by structural bound iron in clay minerals.