

J. Synchrotron Rad. (1999). 6, 394–396

EXAFS investigation of the interaction of hafnium and thorium with humic acid and Bio-Rex70

Melissa A. Denecke,^a D. Bublitz,^a J.I. Kim,^a H. Moll^b and I. Farkes^b

^aForschungszentrum Karlsruhe, Institut für Nukleare Entsorgungstechnik, P.O. Box 3640, D-76021 Karlsruhe, Germany, ^bRoyal Institute of Technology, Dept. of Chemistry, Teknikringen 30, S-10044 Stockholm, Sweden. Email:denecke@ine.fzk.de

The interaction of hafnium(IV) and thorium(IV) with humic acid, HA, is studied using EXAFS and compared to the interaction of these metal ions with carboxylate groups of the cation exchanger Bio-Rex70. Fourier-filtered Hf and Th L₃ edge transmission EXAFS for the first oxygen shell is analyzed. For both Hf(IV)-HA and Hf(IV)-Bio-Rex70, in wet paste and air-dried forms, 6-7 oxygen atoms at R=2.14 Å are found. Th(IV)-HA also exhibits coordination similar to Th(IV)-Bio-Rex70. These observations support conclusions from previous studies on U(VI)-HA that metal cations are sorbed primarily onto HA carboxylate groups; other HA functional groups play a less significant role.

Keywords: humic acids, hafnium, thorium, EXAFS

1. Introduction

Humic acid, HA, is an ubiquitous natural complexing agent that can play an important role in the migration behavior of radionuclides in the environment (see, e.g., Marley *et al.*, 1993; Choppin, 1988; Nash *et al.*, 1981). Only a small number of studies concerning the structure of radionuclide cation species sorbed onto HA have been reported (Denecke *et al.*, 1997; Pompe *et al.*, 1996; Manceau *et al.*, 1996; Sarret *et al.*, 1997). This is surprising because knowledge of the sorbed species structure can extend our understanding of the cation-HA interaction and thereby help improve predictive capabilities of radionuclide transport models used for risk assessments.

Identical structural parameters for the coordination of U(VI) sorbed onto HA were reported by Denecke *et al.* (1997), whereby HA type, preparation conditions, and cation loadings were all varied. This suggests that the same HA functional groups are responsible for binding U(VI). According to IR results and the pH applied for sample preparation, these functional groups are carboxylate groups. Noteworthy is that a U(VI)-HA prepared using a synthetic HA also exhibited the same coordination, despite its having a much higher phenolic OH:carboxylate group ratio than the other HA's investigated, (Denecke *et al.*, 1997; Pompe *et al.*, 1996). This indicates that the HA phenolic OH groups play a subordinate role compared to carboxylate groups in complexing U(VI).

In order to test the hypothesis that HA carboxylate groups are generally responsible for binding metal cations, coordination numbers, N, and bond distances, R, of Hf(IV) and Th(IV) sorbed onto HA were determined from their metal L₃ edge extended X-ray absorption fine structure, EXAFS, spectra. These were compared to those found for Hf(IV) and Th(IV) sorbed onto Bio-Rex70, a cation exchange resin having solely carboxylate groups. If the HA carboxylate groups are responsible for complexing the

metal cations, while HA phenolic OH groups are unimportant, then the structural parameters for Hf(IV) and Th(IV) sorbed onto HA should be the same as those exhibited by these metal cations sorbed onto Bio-Rex70.

2. Experimental

2.1 Sample Preparation

A list of the sorption samples studied and their metal cation-loadings are found in Table 1. All sorption samples were prepared in the following manner. 250 ± 1 mg either purified HA (Aldrich) or protonated Bio-Rex70 (Bio-Rad) were suspended in approximately 35 mL 0.1 M HClO₄ and the pH adjusted to ~2 with NaOH. Five mL of a 0.1 M HClO₄ solution containing 29.5 mM Hf(IV) or 26.2 mM Th(IV) were added and the pH adjusted to ~1.6. The resulting volume of the reaction solution was near 50 mL. The solution was stirred for 66-68 h, at constant pH 1.63±0.05, under ambient conditions. The sample was isolated by centrifugation, washing once with 50mL Milli-Q water. The quantity Hf(IV) or Th(IV) sorbed was determined as the difference between the initial and supernatant concentrations.

Table 1

Sample identification and metal cation loadings for the sorption samples studied.

Sample ID	Sample	Hf(IV) or Th(IV) loading [mg/g sorbent]	Hf(IV) or Th(IV) loading [%PEC] ^a
Hf-B	Hf(IV) sorbed onto Bio-Rex70; air-dried	15.4	3.4
Hf-B-P	Hf(IV) sorbed onto Bio-Rex70; wet paste	"	"
Hf-H	Hf(IV) sorbed onto humic acid; air-dried	85.5	24.5
Hf-H-P	Hf(IV) sorbed onto humic acid; wet paste	"	"
Th-B	Th(IV) sorbed onto Bio-Rex70; air-dried	40.7	6.9
Th-B-P	Th(IV) sorbed onto Bio-Rex70; wet paste	"	"
Th-H	Th(IV) sorbed onto humic acid; air-dried	127.5	28.2
Th-H-P	Th(IV) sorbed onto humic acid; wet paste	"	"

^a PEC, proton exchange capacity, is 10.2 meq/g Bio-Rex70 and 7.8 meq/g Aldrich humic acid. %PEC loaded with cations was calculated assuming 4 eq exchange groups bind to the sorbent to achieve charge neutralization.

For EXAFS measurements, a portion of each sample was placed in wet paste form into a capped 400 µL polyethylene, PE, centrifuge tube. The rest of the sample was air-dried, dispersed in PE powder, and pressed as 1.3 cm diameter pellets. In addition to the sorption samples, polycrystalline tetrakis-acetylacetonate hafnium(IV), Hf(acac)₄, and bis(tetraethylammonium) hexanitratothorium(IV), [(C₂H₅)₄N]₂Th(NO₃)₆, were also prepared as pressed PE pellets.

2.2 EXAFS Measurements

EXAFS spectra were recorded on the Hf and Th L₃ edges, at room temperature, in transmission mode, at the Hamburger Synchrotronstrahlungslabor, HASYLAB, on beamline A1. A Si(311) double-crystal monochromator, detuned 50% of the maximum incident flux, was used. Hafnium L₃ edge spectra were calibrated against the first inflection point in the K edge of a Zn foil defined as 9660.8 eV. L₃ edge spectra of the Th samples

were calibrated in a similar manner using the K edge of a Y foil defined as 17038.0 eV.

The L3 electron ionization energy, E_0 , for all Hf samples was defined as 9565.0 eV; E_0 was defined as 16315 eV for Th samples. Averaged spectra of two or more scans for each sample were analyzed using the suite of programs EXAFSPAK (George *et al.*, 1995). Theoretical oxygen backscattering amplitude and metal-oxygen phase-shift functions, calculated using FEFF7 (Zabinsky *et al.*, 1995), were applied during fits to the data. Theoretical functions were calculated for a 29 atom cluster using either atomic positions for $\text{Hf}(\text{acac})_4$ (Silverton & Hoard, 1963), or those for $[\text{NH}_4]_2\text{Th}(\text{NO}_3)_6$ (Spirlet *et al.*, 1992).

3. Results and Discussion

3.1 Hf and Th L3 EXAFS Spectra

The k^3 -weighted Hf and Th L3 edge spectra and their corresponding Fourier transforms, FT's, recorded for the Hf(IV) sorption samples, $\text{Hf}(\text{acac})_4$, Th(IV) sorption samples, and $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{Th}(\text{NO}_3)_6$, are shown in fig. 1. Visual inspection of the spectra shows that the EXAFS pattern for all Hf(IV) sorption samples is similar, but different from that of the polycrystalline compound. The same is true for the Th(IV) samples. Note that even coordination shells more distant than the first metal-oxygen coordination sphere, visible as FT peaks near 3 Å, are nearly the same in HA and Bio-Rex70 samples.

Table 2

Structural parameters from fits to Fourier-filtered first oxygen shell Hf (top) and Th (bottom) L3 edge EXAFS for $\text{Hf}(\text{acac})_4$, $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{Th}(\text{NO}_3)_6$, and samples of humic acid and Bio-Rex70 treated with Hf(IV) or Th(IV). ΔE_0 was held constant at 8 eV for the Hf sorption samples and at 1 eV for the Th sorption samples.

Sample	Hf-H	Hf-H-P	Hf-B	Hf-B-P	$\text{Hf}(\text{acac})_4$
N	5.8	6.7	7.3	7.4	8.1 (8)*
R [Å]	2.13	2.14	2.14	2.15	2.18 (2.199)*
σ^2 [Å ²]	0.007	0.007	0.009	0.009	0.006
Sample	Th-H	Th-H-P	Th-B	Th-B-P	$[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{Th}(\text{NO}_3)_6$
N	9.9	10.1	9.4	9.4	12.1 (12)*
R [Å]	2.43	2.43	2.44	2.44	2.57 (2.565)*
σ^2 [Å ²]	0.015	0.013	0.013	0.012	0.007

*Values in parentheses are those calculated from the XRD crystal structure determination by Silverton & Hoard (1963) for $\text{Hf}(\text{acac})_4$ and by Spirlet *et al.* (1992) for $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{Th}(\text{NO}_3)_6$.

The back-transformed first peak in the FT of each spectrum was fit to the EXAFS equation using oxygen atoms as backscatterers. Fit results for Hf(IV) and Th(IV) samples are listed in Table 2. The excellent agreement between N and R from EXAFS fits and XRD results for the two polycrystalline compounds substantiates the "correctness" of theoretical phase and amplitude functions used in the EXAFS analysis. For both Hf(IV)-HA and Hf(IV)-Bio-Rex70, in wet paste and air-dried forms, approximately 6-7 oxygen atoms at $R=2.14$ Å are found. Both Th(IV)-HA and Th(IV)-Bio-Rex70 exhibit 9-10 oxygen atoms at 2.43 Å.

Similar coordination numbers and bond distances for metal cation sorption onto both HA and Bio-Rex70 strongly indicates the same type of interaction in both systems. Because Bio-Rex70

only has carboxylate groups capable of cation binding, having the same type of interaction in both systems implicates carboxylate groups responsible for cation binding in HA. If a significant number of HA functional groups other than carboxylate groups were involved, e.g., phenolic OH groups, then interatomic distances would be different and a EXAFS pattern unlike that of their Bio-Rex70 counterparts would be expected.

Results from IR and XPS investigations of the same samples corroborate these conclusions. Observed changes in IR spectra of the HA before and after treatment with Hf(IV) involve bands associated with vibrations of carboxylate groups. XPS measurements show that 4f binding energies for Hf(IV) or Th(IV) sorbed onto HA are identical to that for the corresponding Bio-Rex70 sample. In addition, the $4f_{7/2}$ and $4f_{5/2}$ lines for both HA and Bio-Rex70 sorption samples can be fit with single curves, pointing to a single type of interaction. This information confirms that Hf(IV) and Th(IV) are sorbed primarily onto HA carboxylate groups; other HA functional groups play, at most, a secondary role in metal cation sorption.

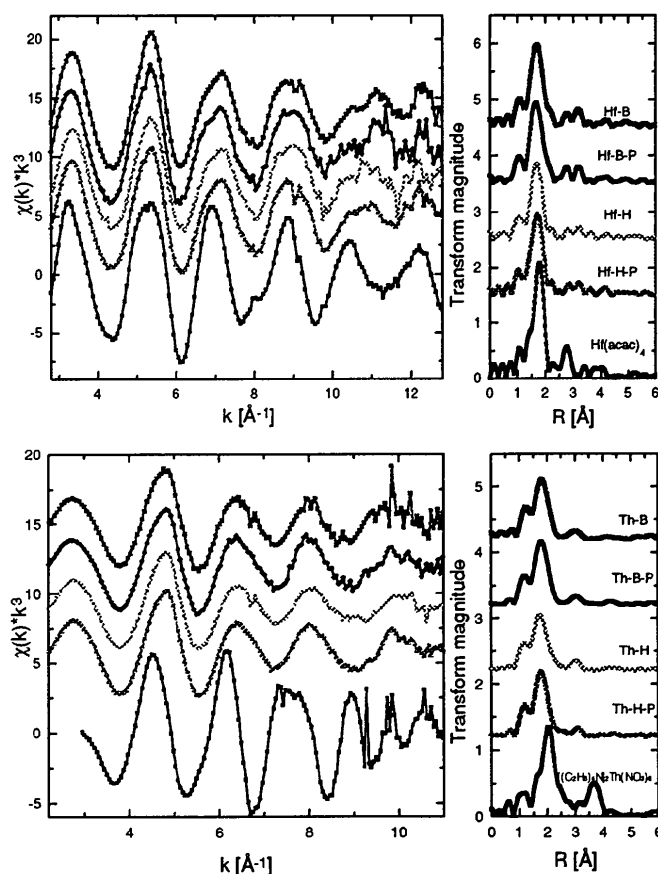


Figure 1
 k^3 weighted Hf (top) and Th (bottom) L3 edge EXAFS (left) and their corresponding Fourier transforms (right) for the Hf(IV) sorption samples, $\text{Hf}(\text{acac})_4$, Th(IV) sorption samples, and $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{Th}(\text{NO}_3)_6$.

4. Conclusion

This EXAFS investigation of the interaction of Hf(IV) and Th(IV) with HA and Bio-Rex70 support the hypothesis that these metal cations are sorbed primarily onto HA carboxylate functional groups. This may allow significant simplification of

models used to predict radionuclide migration via HA-mediated transport in the hydro- and geosphere.

References

- Choppin, G.R. (1988). *Radiochim. Acta* **44/45**, 23-28.
- Denecke, M.A., Pompe, S., Reich, T., Moll, H., Bubner, M., Heise, K.H., Nicolai, R., Nitsche, H. (1997). *Radiochim. Acta* **79**, 151-159.
- George, G.N., Pickering, I.J. (1995). "EXAFSPAK: A suite of Computer Programs for Analysis of X-ray Absorption Spectra", Stanford Synchrotron Radiation Laboratory, Stanford, CA, USA.
- Manceau, A., Boisset, M.C., Sarret, G., Hazemann, J.L., Mench, M., Cambier, P., Prost, R. (1996). *Environ. Sci. Technol.* **30**, 1540-1552.
- Marley, N.A., Gaffney, J.S., Orlandini, K.A., Cunningham, M.M. (1993). *Environ. Sci. Technol.* **27**, 2456-2461.
- Nash, K., Fried, S., Friedman, A.M., Sullivan, J.C. (1981). *Environ. Sci. Technol.* **15**, 834-837.
- Pompe, S., Bubner, M., Denecke, M.A., Reich, T., Brachmann, A., Geipel, G., Heise, K.H., Nitsche, H. (1996). *Radiochim. Acta* **74**, 135-140.
- Sarret, G., Manceau, A., Hazemann, J.L., Gomez, A., Mench, M. (1997). *J. Physique IV* **7**, C2-799-802.
- Silverton, J.V., Hoard, J.L. (1963). *Inorg. Chem.* **2**, 243-249.
- Spirlet, M.R., Rebizant, J., Apostolidis, C., Kanellakopoulos, B., Domberger, E. (1992). *Acta Cryst.* **C48**, 1161-1164.
- Zabinsky, S.I., Rehr, J.J., Ankudinov, A., Albers, R.C., Eller, M.J. (1995). *Phys. Rev.* **B52**, 2995-3009.

(Received 10 August 1998; accepted 15 October 1998)