

Plutonium(III,IV,VI) speciation in Gorleben groundwater using XAFS

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Summary. Pu speciation is investigated by X-ray absorption fine structure (XAFS) at the Pu L_{3} -edge in Gorleben (GoHy) groundwater for Pu added to the groundwater in three different oxidation states (III, IV, VI). The GoHy groundwater stems from an anaerobic aquifer rich in humic substances (HS) (GoHy-532 with ~ 60 – 70 mg/L DOC) and has a neutral pH. Analysis of XANES spectra shows that the samples contain Pu(IV), regardless if Pu(III), Pu(IV) or Pu(VI) is added to the groundwater. The GoHy-532 sample with Pu(VI) added has some Pu(V) and in addition Pu(IV). EXAFS analysis shows Pu–O bond distances to be split into a short and a longer distance. The short Pu–O distance is from bound hydroxy ligands resulting from Pu hydrolysis and/or from bonding to HS phenol groups. A Pu–Pu distance is also found at 3.82–3.85 Å, indicative of hydrolysis and polymeric species formation. Pu(IV) species formed in GoHy-532 are compared to Pu(IV) complexed with fulvic acid (FA) isolated from GoHy-532 at pH_c 1.0 and 1.8. Results indicate that the hydrolysis is less pronounced in the natural groundwater samples than in the Pu(IV)-fulvates prepared from a colloid containing Pu(IV) solution. We observe the Gorleben GoHy and FA apparently stabilize small Pu(IV) hydrolysis species and inhibits precipitation of polynuclear hydrolysis products.

1. Introduction

One important mobilization mechanism of radionuclides released from, *e.g.*, a nuclear waste repository, is colloid mediated transport. Radionuclides can form “eigencolloids” [1] or sorb onto inorganic or organic colloids, thereby remaining mobile under conditions where precipitation or sorption onto minerals would otherwise be expected. The focus of this study is humic colloid mediated actinide transport in groundwater. Humic substance (HS) colloids are ubiquitous in groundwater. Plutonium speciation (*i.e.*, its chemical and physical form) in groundwater samples rich in HS is investigated. The Gorleben (GoHy) groundwater used stems from an anaerobic aquifer rich in HS (GoHy-532 with ~ 60 – 70 mg/L DOC, $E_h = -30$ mV) and has a neutral pH [2].

Speciation of Pu added to GoHy groundwater in three different oxidation states (III, IV, VI) is investigated by X-ray absorption fine structure (XAFS) at the Pu L_3 edge, UV-Vis-NIR absorption spectroscopy and capillary electrophoresis [2]. The Pu oxidation state in the GoHy groundwater after addition is determined from the energy position of their X-ray absorption near edge structure (XANES) spectra. Extended X-ray absorption fine structure (EXAFS) analysis is used to characterize Pu-HS complexes formed and to identify any formation of mixed hydroxo-Pu(IV)-humate species or Pu(IV) polynuclear species. Results are compared to Pu(IV) complexed with purified fulvic acid (FA) isolated from GoHy-532 groundwater [3–5]. The Pu(IV) aqueous species and a precipitated amorphous Pu hydroxide (Pu(OH)₄(am)) sample are used as Pu(IV) reference compounds. As Pu(III) reference, we use an organic Pu(III) complex.

2. Experimental

2.1 Preparation of the samples

A purified Pu stock solution (20 mM Pu in 1 M HClO₄, containing 99.4 wt. % Pu-242 beside small amounts of Pu-238, 239, 240 and 241) is used to prepare the various Pu oxidation states. Pu(III), Pu(IV) and Pu(VI) solutions (*ca.* 10⁻² mol/L) are produced electrolytically according to the method described by Cohen [6]. The concentration of the stock solution for each oxidation state is determined by both liquid scintillation counting (LSC) and UV-Vis-NIR absorption spectroscopy. The latter is also used to verify their oxidation state purity. Samples designated Pu-HS-3, Pu-HS-4, Pu-HS-6 are prepared by adding aliquot of the Pu(III), Pu(IV) and Pu(VI) stock solutions to GoHy-532 groundwater (pH value 6.8) under Ar/1% CO₂ atmosphere. The pH value is readjusted to ~ 7 using 4 M and 1 M NaOH. The final concentrations and pH values are given in Table 1. The Pu concentration in the samples is determined using LSC. An aliquot of each solution is transferred into 400 μ L polyethylene tubes for EXAFS measurements. The Pu-HS-6 sample shows some precipitate formation. This is surprising as we observed no precipitate to form in other, previous experiments under comparable conditions with purified HS. This sample is therefore continuously stirred with a magnetic bar

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Table 1. Characteristics and sample ID of the samples and references investigated.

Sample	Initial Ox. state	pH _c value	[Pu] 10 ⁻³ mol L ⁻¹	Sample form
Pu(III)-BTP	III	–	~ 1	solution
Pu(IV) (aq)	IV	0	1.0	solution
Pu-HS-3	III	6.6–7.0	0.14	solution
Pu-HS-4	IV	6.6–7.0	0.14	solution
Pu-HS-6	VI	6.6–7.0	0.14	solution
Pu-FA-1.0	IV	1.0	1.0 ^a	solid
Pu-FA-1.8	IV	1.8	1.0 ^a	solid
Pu(OH) ₄ (am)	IV	> 2	10.0 ^a	solid

a: Concentration in the reaction solution.

during data acquisition. An aqueous Pu(III) solution reference and a mixed 35 : 65 Pu(III)/Pu(IV) reference sample with a Pu concentration of ~ 1 mM in 1 M HClO₄ are prepared. Unfortunately, both solutions oxidized to Pu(IV) in the time elapsed between preparation and measurement, following transportation to the ESRF. The XANES spectra of these reference samples are identical to the Pu(IV) aquo reference described below. Further details on sample preparation are given in [2].

A 1 mM Pu solution in 1 M HClO₄ containing Pu(IV) aquo ions and an amorphous Pu hydroxide (Pu(OH)₄(am)) are also investigated. Pu(OH)₄(am) is precipitated from a 10 mM Pu(IV) solution in HCl by raising the pH to 2.0 to 2.3. The Pu(OH)₄(am) solid sample is separated from the aqueous solution by ultrafiltration on a cellulose triacetate filter (Amicron, pore size ~ 1.5 nm). The filter with the solid sample is encased in a thin latex bag for measurement.

A 55.5 mM Pu(IV)-242 stock solution used to prepare FA samples is prepared by bubbling NO through a Pu(VI) mother solution (in 1 M HClO₄). The concentration of the mother Pu(VI) stock solution is determined prior to reduction from its UV-Vis absorption spectrum. Utmost care was taken to avoid oxygen in the samples; all of the aqueous reagents are prepared from oxygen free water. The UV-Vis spectrum of the stock solution shows it to contain Pu(IV) eigencolloids. Pu(IV) solution in HClO₄ without added FA turns out not to be stable under the applied conditions; the solutions turn from green to brown, which is an indication that a mixture of Pu oxidation states forms when the solution is left to stand overnight. 75 μL of the Pu(IV) stock solutions are added to two solutions containing approximately 35 mg of isolated FA material in a total volume of ~ 2 mL, adjusted to pH 1.0 and 1.5, and then allowed to react for one day. Following pH readjustment to 1.0 and 1.8, the samples are centrifuged and the separated aqueous phase is pipetted off. The samples are measured in the form of wet solids in their 400 μL centrifuged vials. EXAFS measurements are recorded on these wet, solid samples five to six days after preparation. These samples are designated Pu-FA-1.0 and Pu-FA-1.8, according to the final pH of the reaction solution.

As Pu(III) reference for comparison of Pu *L*₃-edge energy position as a function of valence, we use Pu(III) complexed with *i*-C₃H₇-2,6-di(1,2,4-triazin-3-yl)pyridine (Pu(III)-BTP). For sample preparation, first Pu(III) solution is made by addition of Rongalite (0.06 M) to an aqueous 2 mM Pu(VI)-242 solution in 2 M NH₄NO₃/HNO₃. The

BTP complex is prepared by extracting this freshly made 2 mM Pu(III)-242 solution with a kerosene/octanol solution containing 0.04 M BTP by shaking for 10 min. The organic phase is separated, transferred to a 400 μL vial and these are mounted inside of an inert gas (argon) sample holder for transport and measurement. The Pu concentration in this sample is estimated to be around 1 mM. The sample's Pu *L*₃-edge XANES is recorded within hours of its preparation to avoid oxidation. The direct proximity of the Institute for Nuclear Waste Disposal (INE) controlled area laboratories, where the sample is prepared, and the INE-Beamline at the ANKA synchrotron reduces drastically the delay between preparation and measurement. In this case, we are able to successfully obtain a XANES spectrum for the redox sensitive Pu(III)-BTP sample.

2.2 Spectroscopic investigation

Plutonium *L*₃-edge EXAFS spectra for the Pu(IV) aquo ion and the Pu-HS samples are recorded at the ROBL beamline [7], at the European Synchrotron Radiation Facility (ESRF) storage ring, operating at 6 GeV with a maximal current of 200 mA. Si(111) crystals are used in the double-crystal monochromator (DCM). Higher harmonic rejection is done with two Pt coated mirrors. Pu-HS data are collected at room temperature using a four-element Ge detector manufactured at Lawrence Berkeley National Laboratory in fluorescence mode and an ionization chamber filled with argon gas for transmission.

The EXAFS spectra for the Pu-FA-1.0 and Pu-FA-1.8, the Pu(IV) aquo ion and the Pu(OH)₄(am) reference samples are recorded at the BM12 of the BESSRC CAT at the Advanced Photon Source (APS) in Argonne National Laboratory (ANL). The storage ring is operated at 102 mA, 7 GeV, in top-up mode. Si(111) crystals are used in the DCM equipped with a piezo-driven feedback to stabilize the intensity of the incident X-ray beam [8]. Data are collected in fluorescence mode using a nine-element Ge CANBERRA detector. Argon filled ionization chambers are used here, too.

The Pu *L*₃-edge XANES spectrum for the Pu(III)-BTP complex is recorded at the INE-Beamline for actinide research [9], at the Angströmquelle Karlsruhe (ANKA), Forschungszentrum Karlsruhe, Germany. The storage ring operates at 2.5 GeV with a maximal current of 200 mA. Ge(422) crystals are used in the Lemonnier-type DCM equipped with a piezo-driven feedback to stabilize the intensity of the incident X-ray beam. The data are collected at room temperature in fluorescence mode using a five-element LE-Ge Canberra detector and an argon-filled ionization chamber for transmission.

All spectra are energy calibrated using the first inflection point in the *K*-edge spectrum of a zirconium metal foil, defined as 17998 eV [10]. Data reduction is performed using the code WinXAS 3.0 [11]. XANES spectra are isolated from XAFS scans following subtraction of the pre-edge background absorption, approximated as a linear function, and normalization of the edge jump to unity. While isolating the EXAFS function, $\chi(k)$, the atomic background function $\mu_0(E)$ is optimized with respect to spurious contributions below ~ 1 Å in the *k*²-weighted Fourier transform (FT) of the data. The ionization energy *E*₀ is defined as the max-

imum of the most intense absorption feature – the white line (WL) – in the individual spectra at ~ 18067.5 eV. Neighboring atomic distances R_i , mean square radial displacements or EXAFS Debye–Waller factors σ_i^2 , and coordination numbers N_i for the different coordination shells i are determined using conventional least square fit techniques [12] and the feffit code of the UWXAFS package [13]. Fits are carried out in R space. The overall goodness of the fit evaluated by feffit, given as the “ R factor”, is the sum of squares of the differences between data and model (chi), scaled by the magnitude of data [14]. Theoretical back-scattering amplitude and phase functions for fits to the experimental data are calculated with the multiple scattering code FEFF8.0 [15] using 6–9 atom clusters calculated from structural data for PuO_2 reported in [16].

In order to quantify the WL intensity in XANES spectra, these spectra are modeled with the WINXAS 3.0 software. XANES fits to the experimental data are performed using a pseudo-Voigt (for the WL), a Gaussian (feature near 18105 eV), and an arctan (edge-step) function. The arctan width is set to the natural $\text{Pu } L_3$ line-width, 8 eV [17].

3. Results and discussion

Fig. 1 compares $\text{Pu } L_3$ -edge XANES spectra for all samples. Comparing the energies of XANES features observed for pure valence Pu samples [18] with those of the GoHy samples spectra, we conclude Pu is mainly present as Pu(IV) in Pu-HS-3, Pu-HS-4 and Pu-HS-6, irrespective of which plutonium oxidation state is added to the GoHy groundwater, tri- tetra- or hexavalent. The $\text{Pu } L_3$ -edge energy for all HS samples is shifted to higher energy relative to the Pu(III) reference spectrum energy and is comparable to the energy position for the Pu(IV) reference sample spectra. The Pu-HS-6 XANES exhibits a multiple scattering feature around 18079 eV marked by an arrow in Fig. 1 and, although noisy, visible in the first derivative plot. This feature is characteristic for multiple scattering along the axial oxygen atoms (O_{ax}) comprising the actinyl cation [19], which indicates the presence of plutonyl in sample Pu-HS-6. In addition, the

edge position for Pu-HS-6 is shifted ~ 0.3 eV towards lower energy in comparison to the other HS samples, which also indicates the presence of a most likely Pu(V) “yl” unit, as Pu(V) exhibits edge energies shifted to lower energy relative to their (IV) counterparts [18]. This edge energy trend between tetravalent and pentavalent actinide cations is opposite to what is normally observed: an increase in E_0 with increasing valence state of the absorbing atom is observed. The WL height decrease observed for this sample compared to Pu-HS-3 and Pu-HS-4 is another indicator of the presence of plutonyl [19]. Corroboration of the presence of plutonyl in the Pu-HS-6 sample is provided by EXAFS analysis described below.

The $\text{Pu } L_3$ -edge XANES energy position for the FA samples show that the Pu in the FA complexes remains Pu(IV) . The WL peak height for these samples is significantly decreased compared to the Pu(IV) aquo ion species and is comparable to the WL height of the Pu(OH)_4 (am) precipitate. This is in contrast to what we observed for the HS samples. The intensities of the WL are for all GoHy-532 samples smaller than the WL intensity for the Pu(IV) aquo ion, but much larger than that observed for the amorphous Pu(OH)_4 precipitate. The peak height and peak area variation of the WL is quantified by modeling the $\text{Pu } L_3$ -edge XANES with a XANES fit. The results are given in Table 2. The WL area remains constant within 0.9 units at a mean value of 23.8. However, the WL height is found to vary with sample. A decrease in WL height, without change of the peak area, is ascribed to a change in electronic density of the photoelectron final state without change in valence. In an EXAFS study of Pu(IV) hydrolysis, a WL decrease with constant area is observed during formation of Pu(IV) oxy/hydroxide colloids (polynuclear species) in aqueous solution as a function of pH [1]. The decrease of the WL height is correlated with a colloid size increase, associated with a 6d electron density decrease due to band-width increase with increasing colloid size. Applied to our results, we conclude that the Pu-FA samples, exhibiting low WL heights, contain eigencolloids. We note that the reaction solution for these samples has a 10-fold higher Pu concentration than the Pu-HS samples. In addition, UV-Vis spectra of the Pu(IV)

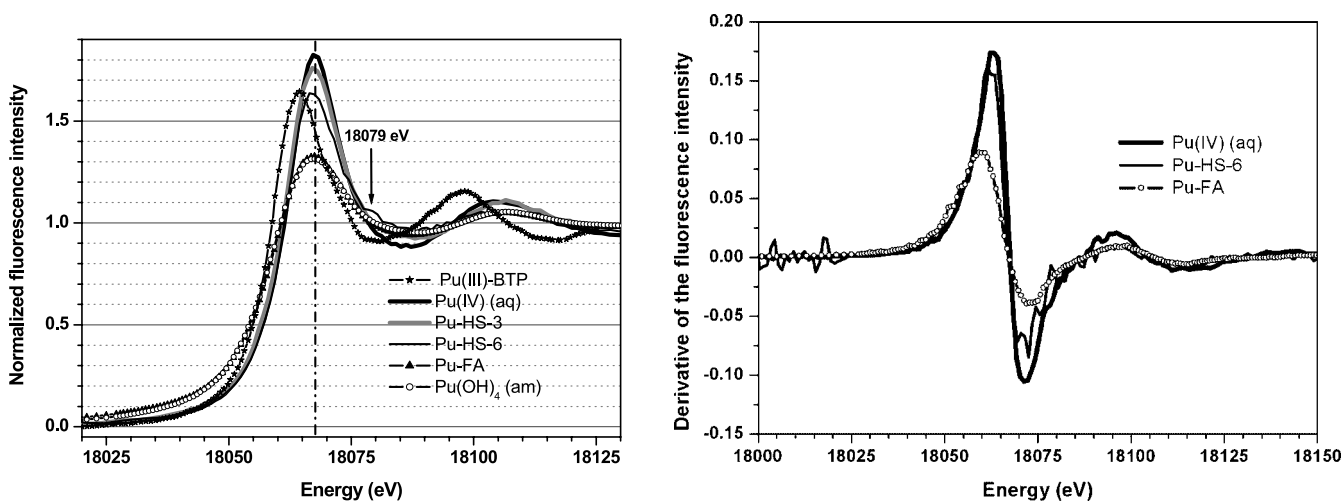


Fig. 1. Left: Comparison of $\text{Pu } L_3$ -edge XANES for the different samples. Pu-HS-3 and Pu-HS-4 have identical spectra, so only Pu-HS-3 is presented. Likewise both Pu-FA samples have identical XANES, so only one is presented. Right: First derivatives of the XANES spectra indicated.

Table 2. Results for the pseudo-Voigt (PV) function in fits to the Pu L_3 -edge XANES in the range of 18 000–18 125 eV.

Sample	Area	WL height	WL energy (eV)
Pu(III)-BTP	24.3	1.50	18 064.4
Pu(IV) (aq)	24.6	1.53	18 067.7
Pu-HS-3	25.1	1.47	18 067.5
Pu-HS-4	24.7	1.48	18 067.7
Pu-HS-6	23.6	1.39	18 067.3
Pu-FA-1.0	23.4	1.00	18 067.7
Pu-FA-1.8	24.1	1.01	18 067.7
Pu(OH) ₄ (am)	24.5	1.03	18 067.7

stock solution used to prepare the FA samples showed it to contain eigencolloids. Obviously the eigencolloids did not dissolve upon dilution and addition of FA, even following the several days spanning sample preparation to EXAFS measurement.

The feature around 18 105 eV lies at higher energy for all samples including Pu(OH)₄(am), compared to that for the Pu(IV) aqueous species. As this feature can be considered the first EXAFS oscillation maximum, its rela-

tive energy position ΔE is a function of bond length, $\Delta E \propto 1/R^2$ [20]. This means that the average Pu–O bond length in all these samples is shorter than in the Pu(IV) aquo species. EXAFS analysis shows this interpretation to be true.

The Pu L_3 -edge EXAFS for the two Pu(IV) reference samples and three Pu-HS samples are shown in Fig. 2. Table 3 lists results of the fits to the experimental data. The metric parameters obtained for the Pu(IV) aquo species solution at $-\log[H^+] = 0$ are in good agreement with the results obtained in previous EXAFS studies [1, 21]; between 8 and 9 oxygen atoms at a mean distance of 2.39 ± 0.02 Å are found.

The Pu–O contribution for the precipitated Pu(OH)₄(am) can be modeled with 4–5 oxygen atoms at a Pu–O distance of 2.32 ± 0.02 Å, but with a large value of σ^2 0.011 Å². This large σ^2 is the source of the broadening of the oxygen FT peak for Pu(OH)₄(am) compared to Pu(IV) aquo. This 2.32 Å Pu–O distance is similar to that expected for PuO₂(cr), but the coordination number is $\sim 40\%$ smaller than the theoretical value of eight expected for PuO₂(cr). This intensity suppression is indicative of strong disorder. Approximately two plutonium atoms are found at a Pu–Pu distance of 3.85 ± 0.02 Å, with a σ^2 value of 0.006 Å² in

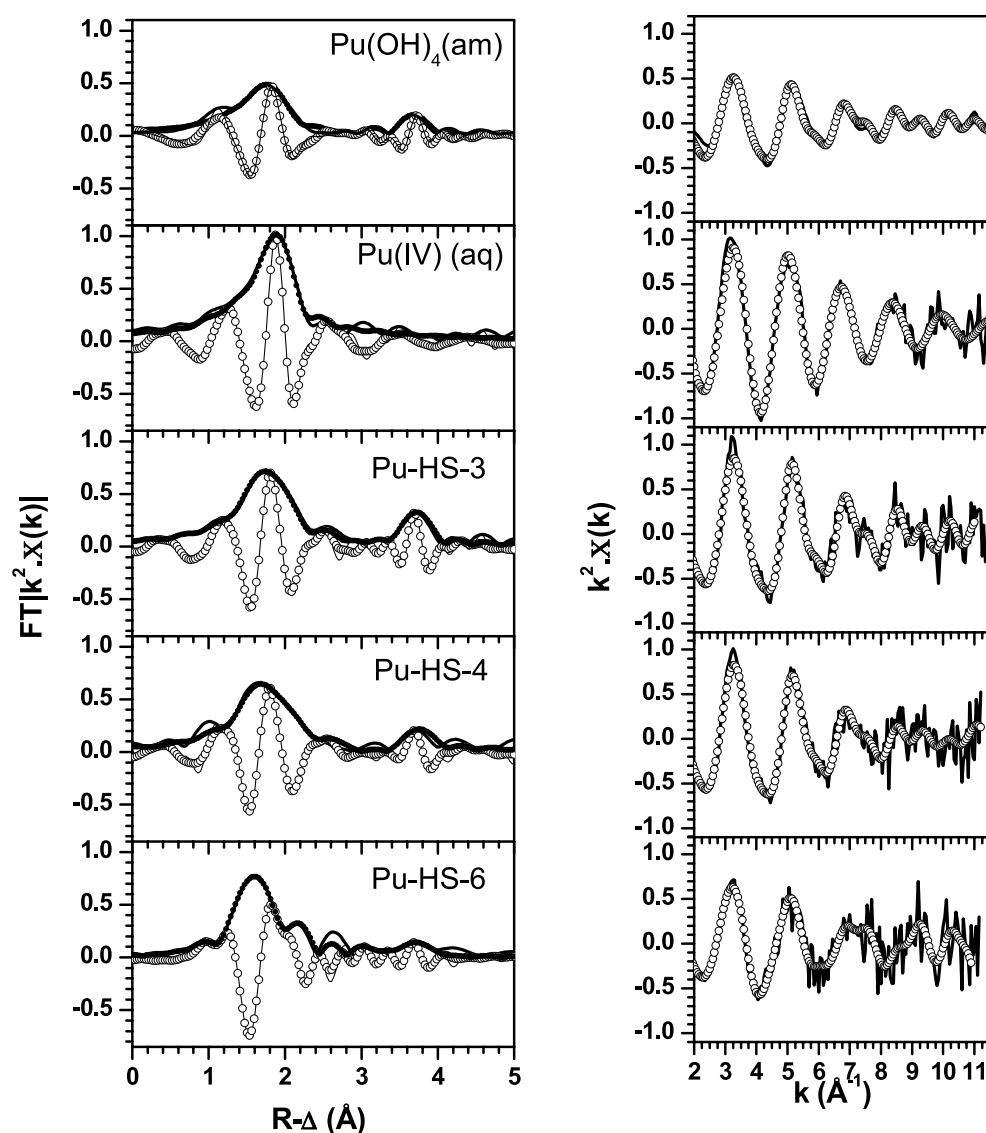


Fig. 2. Pu L_3 -edge k^2 -weighted $\chi(k)$ -functions of the Pu-HS samples and the Pu(IV)(aq) and Pu(OH)₄(am) reference listed in Table 1 (right) and corresponding Fourier transform magnitudes (left). Lines are used for experimental data and symbols for fit results.

$\text{Pu}(\text{OH})_4(\text{am})$. The Pu–Pu distance agrees with that for Pu(IV) eigencolloids reported in [1], but is 0.04 \AA longer than Pu–Pu in $\text{PuO}_2(\text{cr})$ [16, 21].

In contrast to the Pu(IV) aquo ion, the Pu-HS samples show a highly asymmetric oxygen FT peak. It is even more asymmetric than the $\text{Pu}(\text{OH})_4(\text{am})$ oxygen FT peak (Fig. 2). This indicates that more than one distinct Pu–O distance is present. The Pu–O coordination cannot be modeled using a single Pu–O shell, a model with two or three shells must be applied. The results of the fit for both samples Pu-HS-3 and Pu-HS-4 are similar showing 6 to 7 oxygen atoms equally distributed over two Pu–O distances, $2.22 \pm 0.02 \text{ \AA}$ and $2.38 \pm 0.02 \text{ \AA}$. The shorter distance 2.22 \AA is assigned to hydroxyl (O_{OH}) groups in agreement with results in [1] and similar to results for Np(IV) experiments in [22]. These two samples have a higher coordination number of hydroxyl groups than that reported for the Pu colloid samples [1]. This might be attributed to the higher pH value (> 6 in this investigation compared to pH values below 2 in [1]) or may indicate OH coordination through HS phenol group binding.

The presence of a Pu–Pu distance at $R - \Delta$ around 3.75 \AA in the FT indicates the formation of polynuclear species, although HS is present. The FT peak can be well modeled using a single Pu shell with approximately four plutonium atoms at a distance of $3.82 \pm 0.02 \text{ \AA}$. The Pu–Pu distance of $\sim 3.82 \text{ \AA}$ is in good agreement with that in the (Pu–O–Pu) network in $\text{Pu}(\text{OH})_4(\text{am})$ and $\text{PuO}_2(\text{cr})$ [1, 16]. The formation of polynuclear species is not inhibited by the presence of HS in these groundwater samples. However, without HS we would expect a $\text{Pu}(\text{OH})_4(\text{am})$ precipitate to form at these neutral pH values (6.6–7.0) for samples Pu-HS-3 and Pu-HS-4. This is here obviously not the case, as the WL height remains high, an indication that the polynuclear species formed remain small in size, and no precipitate

is observed in these two samples. The HS apparently stabilizes small Pu hydrolysis species in the groundwater, thereby inhibiting their precipitation.

In accordance with the XANES results, our EXAFS analysis shows that the Pu-HS-6 sample has a mixture of different oxidation states, Pu(IV) and plutonyl, likely as Pu(V). To fit the data well, a Pu–O shell at a $\sim 1.80 \text{ \AA}$ distance has to be added to the model, in order to take into account the presence of a small amount of plutonyl cations. The contribution of O_{ax} of the “yl” species is small, 0.4 oxygen atom at a Pu–O distance of $1.80 \pm 0.02 \text{ \AA}$. This distance lies between the distance for the Pu(V) aquo ion (1.84 \AA) and that for Pu(VI) aquo ion (1.74 \AA) [16]. The longest Pu–O distance found at $2.51 \pm 0.02 \text{ \AA}$ is associated to the equatorial atoms (O_{eq}) of the plutonyl species. This observed distance is slightly longer than that for the plutonyl Pu(V) or Pu(VI) aquo ion (2.45 \AA) [16]. The Pu(IV) species in Pu-HS-6 has a mean Pu–O distance of $2.29 \pm 0.02 \text{ \AA}$ with a coordination number of ~ 3 . Again we assume this relatively short Pu–O distance is associated with the presence of hydroxyl bonding to Pu(IV). However, this actual 2.29 \AA Pu–O distance is longer than those in the Pu-HS-3 and Pu-HS-4 samples. This is due to the fact that this is an averaged Pu–O distance, accounting for the short $\sim 2.20 \text{ \AA}$ distance attributed to hydroxyl and a $\sim 2.38 \text{ \AA}$ distance of the remaining Pu–O bonds. The EXAFS k range available did not allow us to distinguish between the two shells.

The Pu L_3 -edge EXAFS for the two Pu-FA samples are depicted in Fig. 3. Both Pu-FA samples show reduced EXAFS and FT intensities compared to the reference samples and to the Pu-HS samples. The oxygen FT peak is split into two Pu–O distances. The structural parameters obtained are very similar to the Pu(IV) oxy/hydroxide colloids at comparable pH values, but without FA [1]. The fit results for both Pu-FA-1.0 and Pu-FA-1.8 samples (Table 3)

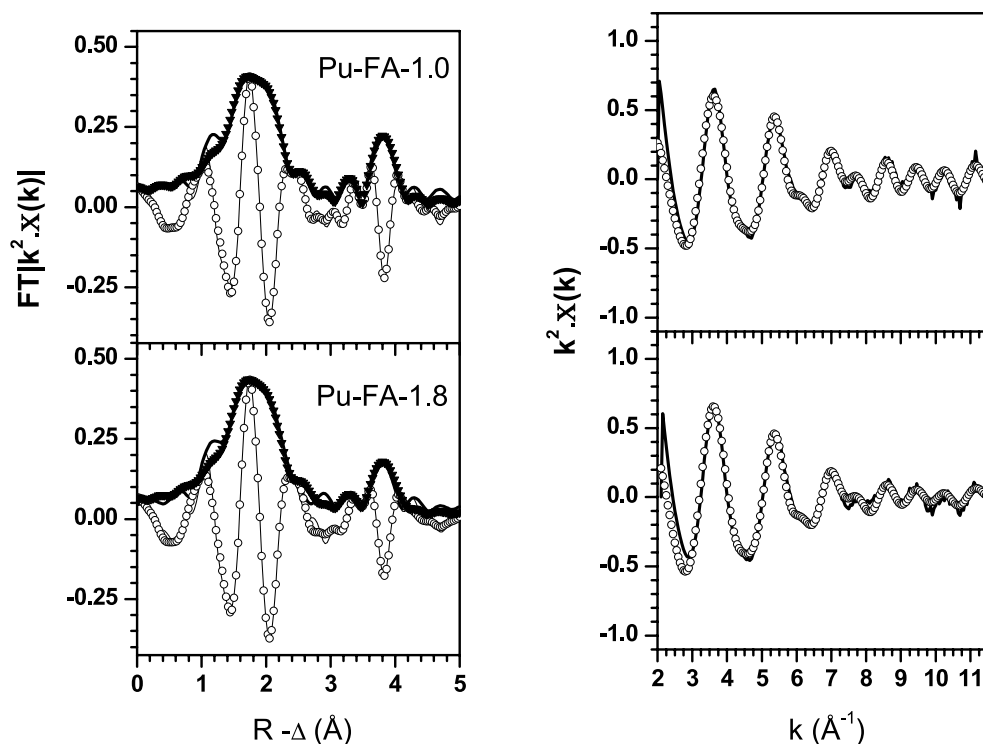


Fig. 3. Pu L_3 -edge k^2 -weighted $\chi(k)$ -functions for the Pu(IV)-FA samples listed in Table 1 (right) and corresponding Fourier transform magnitudes (left). Lines are used for experimental data and symbols for fit results.

Table 3. Results of the fits to the EXAFS data.

Samples	Shells	N	R [Å]	σ^2 [10^{-3} Å ²]	ΔE_0 [eV]	R factor [%]
Pu(IV) (aq)	O	7.8	2.39	7.2	-0.2	0.3
Pu-HA-3	O _{OH}	3.0	2.23	1.0	0.09 ^a	2.4
	O	3.4	2.38	1.0		
	Pu	4.2	3.82	6.7	1.70 ^b	
Pu-HA-4	O _{OH}	3.1	2.22	1.0	0.09 ^a	1.6
	O	3.4	2.39	1.4		
	Pu	4.5	3.82	6.7	1.70 ^b	
Pu-HA-6	O _{ax}	0.4	1.80	1.0	3.59	2.2
	O	3.1	2.29	1.0		
	O _{eq}	2.9	2.51	1.7		
	Pu	1.2	3.85	10.8	6.15	
Pu-FA-1.0	O _{OH}	1.0	2.19	1.0	10.1 ^c	0.3
	O	3.2	2.37	6.2		
	Pu	2.6	3.84	7.0	12.0 ^d	
Pu-FA-1.8	O _{OH}	0.8	2.18	1.0	10.1 ^c	0.7
	O	4.1	2.36	9.2		
	Pu	2.8	3.84	10.3	12.0 ^d	
Pu(OH) ₄ (am)	O	4.6	2.32	11.3	0.3	1.5
	Pu	2.2	3.85	6.1	0.9	

a–d: constrained to the same value for both samples.

are similar; 4 to 5 oxygen atoms are found distributed over two Pu–O distances, 2.19 ± 0.02 Å and 2.37 ± 0.02 Å. The shorter 2.19 Å distance is again assigned to hydroxyl groups. The apparent total oxygen coordination number obtained for the Pu-FA-1.0 samples of ~ 4 appears low, it is smaller than for Pu-FA-1.8 and for Pu(OH)₄(am).

The Pu–Pu distance at $R - \Delta$ around 3.80 Å in the FT for the Pu-FA samples indicates the existence of polynuclear species, even though FA is present. The FT peak can be well modeled using a single Pu shell with approximately 2–3 plutonium atoms at a distance of 3.84 ± 0.02 Å. As for the Pu-HS samples, this is in good agreement with the Pu–Pu distance of the (Pu–O–Pu) network in Pu(OH)₄(am) and PuO₂(cr) [1, 16]. Again we interpret that the presence of this Pu–Pu distance implies that polynuclear species are stabilized by FA. This is in accord with the XANES interpretation discussed above that these samples contain eigencolloids.

4. Conclusion

Plutonium speciation in Gorleben groundwater with Pu added in three different oxidation states (III, IV, VI) using Pu L_3 -edge XAFS shows that the Pu is present mostly as Pu(IV) regardless which Pu valence (Pu(III), Pu(IV) or Pu(VI)) is added. The GoHy-532 sample with Pu(VI) added exhibits the presence of a minor portion of plutonyl cations, as revealed by the Pu–O distance ascribed to axial “yl” oxygen atoms. Most likely plutonyl is present as Pu(V).

Comparison of the results for Pu in groundwater with those from Pu(IV)-FA samples prepared at pH 1.0 and 1.8

shows that the polymerization of Pu hydrolysis species is less pronounced in the natural groundwater samples than in the Pu(IV)-fulvates. This, however, is likely due to the higher overall Pu concentration used in the FA experiments compared to the groundwater experiments and the fact that the stock solution used in the preparation of the Pu-FA samples contained Pu(IV) eigencolloids. Obviously these eigencolloids did not dissolve after dilution and following nearly week storage in the presence of FA. The Pu-HS samples have a higher coordination number of hydroxyl groups, compared to polynuclear species formed in absence of HS. This can be attributed to the higher pH value of the groundwater and/or to contribution of phenol groups to the Pu(IV) bonding. This study shows that humic and fulvic acid appear to stabilize small Pu(IV) polynuclear hydrolysis species and inhibit precipitation of hydrolysis products. The notable exception in this investigation is the sample with Pu(VI) added, which contained persistent plutonyl cations, in addition to Pu(IV). The reason why this particular sample formed a precipitate remains to be resolved.

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