A combined XAFS, ESI TOF-MS and LIBD study on the formation of polynuclear Zr(IV), Th(IV) and Pu(IV) species

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Abstract. The long term radiotoxicity of spent nuclear fuel disposed of in deep underground repositories after discharge from nuclear power reactors is determined by actinide elements, mainly plutonium. Water intrusion into the repository might cause container corrosion and leaching of the waste matrices, leading to the release of Pu and other actinides into the geological environment. Performance assessment for a future nuclear waste repository requires detailed knowledge on actinide aqueous chemistry in the aquifer surrounding the disposal site. Tetravalent actinides exhibit a strong tendency towards hydrolysis and subsequent polymerization and/or colloid formation. These species provide a potential pathway for migration of actinides away from the repository. Therefore, it is of fundamental interest to study their generation and properties in-situ. To this end, X-ray Absorption Fine Structure Spectroscopy (XAFS) at the INE-Beamline for actinide research at ANKA, Electrospray Mass-Spectrometry (ESI TOF-MS) and Laser Induced Breakdown Detection (LIBD) are combined at FZK-INE in a comprehensive attempt to characterize Zr(IV) (An(IV) analogue), Th(IV) and Pu(IV) polymerization and colloid formation.

1. Introduction

Final disposal strategies for spent nuclear fuel in underground waste repositories without prior reprocessing have to ensure safe containment of radiotoxic, long lived actinide elements, mainly plutonium, over geological time scales. Most failure scenarios consider water intrusion into the repository as eventually causing container corrosion and leaching of the waste matrices, leading to the release of actinides into the geological environment. Tetravalent actinides (An(IV)) exhibit a remarkably complex aqueous chemistry. They are well known for their strong tendency towards hydrolysis (i.e., complexation with OH⁻ ligands) and subsequent polymerization or ‘eigencolloid’ formation. These species might be highly mobile in the aquifer surrounding the repository, thus providing a potential pathway for An(IV) migration away from the disposal site.

For several reasons, properties of zirconium polyspecies in aqueous solutions have found renewed interest over the last few years in the context of nuclear waste disposal. Zr metal is used as a fuel-cladding material in nuclear light water reactors and Zr has a high yield among uranium fission products. In solubility and hydrolysis studies, Zr(IV) is considered as inactive An(IV) analogue. It became evident that the Zr⁴⁺ cation is stable only under very acidic conditions (pHc = -log[H⁺]<0) and that mononuclear hydroxide complexes dominate only in very dilute solutions ([Zr(IV)]<10⁻⁵ M). At higher concentrations or lower acidities, the solvated Zr⁴⁺ ion ([Zr⁴⁺·8H₂O]) hydrolyzes and forms...
\([\text{Zr(OH)}_3\cdot7\text{H}_2\text{O}^{-}}\) and \([\text{Zr(OH)}_2\cdot6\text{H}_2\text{O}^{-}}\) complexes. Condensation of the latter complex through formation of OH⁻ bridges (olation) leads to polymerization and the formation of cyclic tetramers \([\text{Zr}_4(\text{OH})_8\cdot16\text{H}_2\text{O}^{-}}\), e.g., [1]. Tetramers and similar polynuclear species account for the largest mass fraction of Zr in solution.

Hydrolysis and polymer formation of Th(IV) in solutions is of continuing interest due to the possible relevance of Th as fuel in future nuclear power cycles, as well as for its role as Pu(IV) analogue [2]. In acidic solutions, Th forms tetravalent ions, Th⁴⁺, coordinated by ~11-12 water molecules, e.g., [3]. It is widely accepted that close to the solubility limit of \(\text{Th(OH)}_4(\text{am})\), polynuclear hydroxide complexes exist. However, except for the dimer, which was detected directly [4], information on these polymers was only deduced indirectly from titration data. When the solubility is exceeded, nm sized colloids, which were subject to a considerable number of investigations, e.g., [5], are formed. At near neutral pH the presence of colloids increases the apparent solubility of \(\text{Th(OH)}_4(\text{am})\) by almost two orders of magnitude [6]. However, the role of polynuclear hydroxide complexes in the formation process of these colloids is not well understood.

The Pu⁴⁺ cation hydrolyzes readily, even under very acidic conditions [7] and the resulting monomeric hydroxide complexes form polynuclear species at Pu(IV) concentrations \(>10^{-6}\) M [8]. It is frequently assumed that hydrolysis of mononuclear Pu(IV) species is the first step towards colloid formation. As for Th(IV), the role of Pu(IV) polynuclear complexes preceding these colloids is not yet clear. Their existence is generally accepted, e.g., [9] and it is assumed that formation processes involve hydroxide (olation) or oxygen (oxolation: \(2\text{OH}^{-}\rightarrow\text{H}_2\text{O} + \text{O}^{2-}\)) bridging of Pu nuclei. In recent reviews, e.g. [10], Pu(IV) polynuclear species were not considered as thermodynamically stable and a model which describes the formation of colloids from mononuclear hydroxide complexes \([\text{Pu(OH)}_n^{4-n}]\) was favored. Alternatively, a model presented in [11] describes the formation of colloids in acidic solutions from cubic monomers \((\text{Pu(OH)}_2(\text{H}_2\text{O})_6^{2+})\) forming edge sharing dimers, trimers and larger polynuclear complexes by hydrolysis and oxolation. Further condensation of \([\text{Pu}_x\text{O}_y(\text{OH})^{6y-2x}(\text{H}_2\text{O})_z]\) polymers culminates in the formation of large colloids with an ordered fcc (face-centered-cubic) Pu–O–Pu backbone structure detected by Pu L₃-EXAFS.

2. Experimental

2.1 Sample preparation

Samples of \([\text{Zr(IV)}]=1.5-10\ \text{mM}\) at \(0<p\text{H}_C<3\) were prepared by dissolving appropriate amounts of zirconyl chloride in hydrochloric acid with a predefined pHₐ. Zirconyl chloride hydrate \((\text{ZrOCl}_2\cdot3\text{H}_2\text{O, 99.99%})\) was used without further purification. The hydrochloric acid was prepared by diluting HCL (37%, analytical grade) with ultrapure Milli-Q water (18.2 MΩcm). No additional electrolyte was added. The solutions were kept in an ultrasonic bath for at least 15 min and allowed to equilibrate for at least one hour prior to the measurements. The pHₐ of the final solution was measured using a combination glass electrode calibrated against standards of 1 M, 0.1 M, 0.01 M and 1 mM HCl without additional electrolyte. The Zr concentrations of all samples were measured by ICP-MS with a precision <2%.

Amorphous \(^{232}\text{Th(IV)}\) hydroxide was precipitated by neutralization (addition of NaOH) of a thorium nitrate solution in HClO₄, centrifuged and washed with distilled water/ethanol several times. The precipitate was redissolved in hydrochloric acid, resulting in a stock solution of \([\text{Th(IV)}]_{\text{tot}} = 3.6 \times 10^{-1}\) M at pHₐ 3.0. Samples at concentrations between \([\text{Th(IV)}]_{\text{tot}} = 2 \times 10^{-4}\) M and \(1.2 \times 10^{-1}\) M below or close to the solubility limit of \(\text{Th(OH)}_4(\text{am})\) were prepared by appropriate dilution of the stock solution with hydrochloric acid and/or very slow titration (~10μl/min) with Milli-Q water under vigorous stirring in order to prevent colloid formation due to local oversaturation. No electrolyte was added, i.e., the ionic strength of the samples was defined by the concentration of hydrochloric acid and by the Th(IV) hydrolysis products only. All samples were prepared and stored in quartz cells.

A \(^{242}\text{Pu(IV)}\) stock solution in 0.5M HClO₄ was repeatedly fumed with HCl, electrolytically reduced to Pu(III) and subsequently oxidized to Pu(IV) under UV-Vis spectrometric control. Care was taken to achieve colloid free solutions. From these stock solution, samples were prepared at constant ionic
strength (I = 0.5 M, HCl/NaCl) by slow titration (10 μl/min) of the stock solution with appropriate amounts of Milli-Q water, HCl, and NaOH. After 5–12 h equilibration time the samples were measured by XAFS, LIBD and UV-Vis absorption spectroscopy.

2.2 LIBD and ESI TOF-MS

Laser-Induced Breakdown Detection LIBD is a sensitive method for colloid detection in solution. In An(IV) aquatic chemistry studies LIBD was originally used to detect the onset of colloid formation upon crossing the solubility threshold. The method was further developed to allow determination of particle size distributions in colloidal suspensions with particle diameters between about 10 and 400 nm by S-curve analysis, cf. [12]. The Electrospray Time-Of-Flight Mass Spectrometer (ESI TOF-MS) used for polymer characterization is described in detail in [13]. It consists of a home built nanospray ion source equipped with spray capillaries with inner tip diameters of 2 μm. The sample flow is approximately 10 nl/min. Droplets D<100 nm in diameter form and shrink within a few microseconds to tiny droplets of some 50 water molecules, each containing only one hydroxide complex (\([\text{M(IV)}_{x}(\text{OH})_{4x-y}m\text{Cl} \cdot n\text{H}_2\text{O}]^{4x-y-m}\), M = Zr, Th, Pu - denominated \((x,y)m\) in the following). The ions are analyzed in the time-of-flight mass-spectrometer with a maximum mass resolution of \(m/\Delta m = 26000\) which provides isobaric resolution and allows pH-dependent identification of polymerization \(x\) as well as the number of hydroxide groups \(y\) and via \(z = 4x-y\) the charge of each oligomer.

2.3 XAFS spectroscopy

Samples containing An(IV) polymer species were investigated by XAFS spectroscopy at the Ångstromquelle Karlsruhe (ANKA), Forschungszentrum Karlsruhe, Germany, at the INE-Beamline for actinide research [14]. For Zr K and Pu L3 measurements the spectra were calibrated against the first inflection point in the XANES of Zr metal (assigned as 17.998 keV), for Th L3 measurements against the XANES of Y metal (inflection point assigned as 17038 eV). For samples with metal concentrations > 10 mM the transmission signal recorded with Ar-filled ionization chambers at ambient pressure was analyzed. Samples with lower concentrations were measured in fluorescence detection mode by registering the Zr Kα or Th/Pu Lα fluorescence yield using a five-pixel Ge solid state detector (Canberra LEGe). Up to 8 scans were collected at room temperature and averaged for each sample. XANES spectra as depicted in figure 3a were isolated from XAFS scans following subtraction of the pre-edge background absorption and normalization of the edge jump to unity. EXAFS data analysis (cf. [13] and references therein) was based on standard techniques using the ATHENA (v0.8.050) and the UWXAFS software packages. \(E_0\), the origin used to calculate the EXAFS \(\chi(k)\) functions, was fixed at the maximum of the first-derivative in the Zr K-XANES and at the white line (WL) maximum positions for Th L3- and Pu L3-XANES, respectively. EXAFS fit parameters (neighboring atom distances \(R_i\), EXAFS Debye-Waller factors \(\sigma_i^2\) and coordination numbers \(N_i\) for coordination shell i) were determined using the feffit code (v2.98). Backscattering amplitude and phase shift functions for single scattering paths were calculated for a 30-atom cluster of tetragonal ZrOCl\(_2\)×8H\(_2\)O, a 45-atom ThO\(_2\) cluster with fluoride structure and a 45-atom PuO\(_2\) cluster with fluoride structure using FEFF8.2 for Zr K-, Th L3- and Pu L3- EXAFS analysis, respectively. Prior to analysis, the \(k^2\)-weighted Zr K-, Th L3- and Pu L3-EXAFS was Fourier-transformed over a \(k\)-space range of \(2.5–13 \text{ Å}^{-1}\), using symmetric square windows with \(\Delta k = 0.2 \text{ Å}^{-1}\) “Hanning sills”. All fit operations were performed in R-space. The amplitude reduction factor \(S_0^2\) was fixed at 0.9 for Zr K spectra. This value has been derived for EXAFS analysis of crystalline ZrOCl\(_2\)×8H\(_2\)O in [15] to reproduce the Zr next-neighbor coordination numbers. The value has been fixed at 1.0 for Th and Pu measurements.
3. Results and Discussion

ESI TOF-MS revealed that with increasing pHc the fraction of Zr(IV) monomeric species at [Zr] = 10 mM decreases and oligomeric species form, which contain an increasing number of Zr(IV) ions (figure 1). Pentamers and larger complexes form at the expense of tetramers, resulting in a complex mixture of many solution species [13]. No dimers or trimers are observed. Surprisingly, at pHc > 1.7 the number of species decreases and the octamer accounts for more than 70% of the detected ions. The Fourier transformation (FT) of the EXAFS obtained for samples at pHc 0.1 and pHc 0.4 exhibits peaks centred at ~1.7 Å (R-Δ, i.e., R~2.2 Å radial distance), corresponding to Zr-O backscattering, and less pronounced peaks centred at ~3.1 Å (R-Δ, i.e., R~3.6 Å radial distance), due to Zr-Zr backscattering. The metrical parameters derived by fit analysis are a strong evidence for the presence of tetramers (cf. [2]). This observation is in good agreement with the 80% relative abundance of the tetramer found by ESI TOF-MS at high acidity. At pHc > 0.5 the percentage of pentamers with different RZr-Zr increases. Accordingly, in the EXAFS spectra the Zr-Zr scattering peak eventually vanishes (samples at pHc = 0.6-1.2). Based on the EXAFS data alone, one might erroneously conclude from the absence of a Zr backscattering signal that mononuclear Zr hydroxide complexes (Zr(OH)_{y}^{4-y}) prevail under these conditions. However, the vanishing Zr-Zr can only be explained by destructive interference due to multiple Zr-Zr distances. This interpretation is strengthened by the result obtained for the pHc 1.8 sample: according to ESI TOF-MS the number of different solution species is strongly reduced and octamers account for more than 70% of the Zr solution species. Consequently, the distinct Zr-Zr backscattering signal appears again in the EXAFS. Fit parameters (increase of N_{2(Zr)}) are in agreement with the dominance of octamers which are formed by stacking of two tetramers. The Zr K-XANES of these samples exhibits significant differences between the [Zr] = 10 mM and a [Zr] = 1.5 mM sets. The former series shows an ongoing decrease of the WL intensity with increasing pHc, the latter exhibit constant peak heights, independent of pHc. WL intensity decrease and/or WL broadening in these sample systems were found to be generally associated with increasing condensation of the aquatic metal oxide/hydroxide species, i.e., the transition from a hydrated or hydrolyzed ionic species to oligomeric and colloidal species with bulk-like properties (cf. [3] and the Pu results shown below). According to this interpretation, Zr oxide/hydroxide species seem to be generally smaller in the low concentration series compared to the high concentration series.

**Figure 1.** Species distribution according to ESI TOF-MS (relative number of detected ions) at [Zr(IV)]_{tot} = 10 mM. p denotes the degree of nucleation, e.g., p=8 for octamers.

**Figure 2.** Th L3-EXAFS at [Th(IV)]_{tot}=15.9 mM, pHc 3.46 (70% pentamers): (a) FT magnitude (solid line), fit magnitude (open circles), FT real part (thin solid line) and fit real part (open triangles); (b) raw data (solid line) and fit (open circles) in k-space.
The formation of polynuclear thorium hydroxide complexes in acidic aqueous solutions was observed by ESI TOF-MS by repeated measurements over a time span of up to one year. It was found that at concentrations above $[\text{Th(IV)}]_{\text{tot}} = 10 \, \text{mM}$ pentamers and dimers are the dominant stable species. In contrast, the fractions of pentamers initially present at $[\text{Th(IV)}]_{\text{tot}} \approx 0.2 \, \text{mM}$ decreased within less than four weeks, while the formation of nm sized colloids was detected by LIBD [16]. In agreement with these results, Th L3-XAFS spectra taken from fresh samples (i.e., within one day after preparation) were free of characteristic particle size effects (i.e., WL dampening and broadening). Hence, metal-metal distances detected by XAFS have to be attributed to the existence of polymeric species. At $[\text{Th(IV)}]_{\text{tot}}=0.68 \, \text{mM}$ and $\pH \leq 3.67$, 44% of the Th in solution formed $(5,17)$-pentamers according to ESI TOF-MS, while 56% of Th was present as monomers. Two coordination shells are discernable in the EXAFS FT of this sample. The first one around 1.9 Å (R–Δ) reflects Th bonding to bridging and terminal hydroxide groups and to oxygen from terminal water. The Th-O distance spread requires two oxygen shells in the fit. The shorter distance (3.8 O at 2.40 Å) is attributed to bridging and terminal OH- groups, the longer (3.4 O at 2.55 Å) to terminal water. The average oxygen coordination number (7-8) is significantly reduced compared to the aquo ion (~11 O at 2.45 Å). Assuming an average of 8 oxygen neighbors for each Th atom in the pentamer, one would expect a somewhat larger value of 9-10. The well resolved second shell around 3.7 Å (R–Δ) reflects backscattering from Th neighbors in the pentamers. Only one Th-Th distance is discernible from the data. The fit yields 1.7 Th at 3.87 Å, which is in accordance with the assumption of Th having 2 or 4 second next Th neighbors in the pentamer and none such in the monomer. $N_{\text{Th(2)}}$ is found to be slightly increased for the sample at $[\text{Th(IV)}]_{\text{tot}} = 1.0 \, \text{mM}$, $\pH \geq 3.55$ as expected due to the increase of pentamers to 60%. Fit results for a sample at $[\text{Th(IV)}]_{\text{tot}}=10 \, \text{mM}$ are shown in figure 2. For this sample ($[\text{Th(IV)}]_{\text{tot}}=15.9 \, \text{mM}$, $\pH \leq 3.46$, 70% pentamers) we observed a significant increase of $N_{\text{Th(2)}}$ (3.1 Th at 3.94 Å), reflecting the increasing polymerization in this concentration range. The Th-O coordination (8.8 O at 2.49 Å - no splitting, but a larger Debye-Waller factor of 0.013 Å²) is in full accordance with assumption of the average contribution of $N_{\text{O(1)}} \approx 11$ for 30% monomers and $N_{\text{O(1)}} \approx 8$ for 70% pentamers to the EXAFS.

Combining ESI TOF-MS, quantum chemical cluster calculations, Th L3-EXAFS and HEXS measurements, a structural model of the Th(IV) pentamer has been conceived based on two dimers linked by a central Th(IV) cation. Details will be presented in a forthcoming publication [17].

Figure 3. (a) Normalized Pu L3-XANES spectra of a sample series containing $[\text{Pu(IV)}]_{\text{tot}} \approx 0.16 \, \text{mM}$. The inset shows the XANES at $\pH = 0.2$ with a box marking the enlarged area shown in the comparison; (b) WL peak heights (left) and Pseudo-Voigt profile areas for these samples.

Figure 3a shows the normalized Pu L3-XANES derived for samples from a series containing $[\text{Pu(IV)}]_{\text{tot}} \approx 0.16 \, \text{mM}$. The spectral range shown here is a zoom into the WL area near the absorption edge. The spectral trend becomes more obvious considering the corresponding WL peak heights and Pseudo-Voigt profile areas depicted in figure 3b. The bending for $\pH \geq 0.7$ of the curves coincides with the beginning of colloid formation in the Pu(IV) suspensions detectable by LIBD. Although structurally slightly different, no relevant changes are discernable from a comparison of the XANES.
derived for fresh colloids (pHc 1.8) and a corresponding suspension aged for two years. In the FT representation of Pu L3-EXAFS data obtained for these samples, two coordination shells are discernable. The first one around 1.7 Å (R-Δ) reflects Pu bonding to bridging oxygen atoms and to oxygen from terminal water and hydroxide units. As for Th(IV), these different oxygen neighbours exhibit a spread of bond distances leading to large Debye-Waller factors or requiring inclusion of two oxygen shells or asymmetry parameters (3rd cumulants) in the fit. The second shell around 3.5 Å (R-Δ) reflects backscattering from Pu neighbors in the polymer. The decrease of the Pu-Pu distance and the increase of Pu and O coordination numbers observed for the aged sample indicate a ripening of the amorphous oxide/hydroxide polymers present in sample 8 towards crystalline colloids with fluorite-like structure (PuO2: RPu−O = 2.32 Å, RPu−Pu = 3.81 Å, NO(1) = 8) [18].

Investigation of different undersaturated Pu(IV) suspensions with varying pHc, [Pu(IV)]tot and time span between sample preparation and XAFS data acquisition revealed that in most cases a distinct Pu backscattering signature in the EXAFS signal was hardly observable, although the presence of small polymers was unambiguous from ESI TOF-MS [18]. In contrast to analogue applications on Th(IV) and Zr(IV) solutions (cf. the discussion above), EXAFS seems to be less suited for observing the polymerization processes in such solutions. However, as previously assumed for Zr(IV) polymerization, simultaneous presence of different metal-metal distances - equivalent with a high degree of disorder - causes destructive interference of scattering and an extinction of the corresponding backscattering signal. This effect was demonstrated by simple simulations performed with FEFF8.2 for (a) an ideal three-shell PuO2 (fluorite structure) cluster and (b) a cluster with empty Pu sites and Pu atoms shifted to achieve an arbitrary spread δRPu−Pu of ±0.15Å around the crystallographic value of RPu−Pu=3.81 Å. From the missing Pu backscattering peak expected at ~3.5 Å in the simulation of the distorted and defect cluster we concluded that metal cation voids and coexistence of several metal-metal distances are sufficient to explain destructive interference of the backscattered waves to entirely suppress the An(IV) backscattering signal in the EXAFS of polymeric or colloidal species.

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