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Stabilization of polynuclear plutonium(IV) species by humic acid

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Abstract

Although the formation of tetravalent plutonium (Pu(IV)) polymers with natural organic matter was previously observed by spectroscopy, there is no quantitative evidence of such reaction in batch experiments. In the present study, Pu(IV) interaction with humic acid (HA) was investigated at pH 1.8, 2.5 and 3, as a function of HA concentration and for Pu total concentration equal to 6×10^{-8} M. The finally measured Pu(IV) concentrations ($[\text{Pu(IV)}]_{\text{aq}}$) are below Pu(IV) solubility limit. Pu(IV)-HA interaction can be explained by the complexation of Pu(IV) monomers by HA up to $[\text{Pu(IV)}]_{\text{aq}} \sim 10^{-8}$ M. However, the slope of the log-log Pu(IV)-HA binding isotherm changes from ~ 0.7 to ~ 3.5 for higher $[\text{Pu(IV)}]_{\text{aq}}$ than $\sim 10^{-8}$ M and at any pH. This result suggests the stabilization of hydrolyzed polymeric Pu(IV) species by HA, with a 4:1 Pu:HA stoichiometry. This confirms, for the first time, previous observations made by spectroscopy in concentrated systems. The humic-ion binding model, Model VII, was introduced into the geochemical speciation program PHREEQC and was used to simulate Pu(IV) monomers binding to HA. The simulations are consistent with other tetravalent actinides-HA binding data from literature. The stabilization of a Pu tetramer ($\text{Pu}_4(\text{OH})_8^{8+}$) by HA was proposed to illustrate the present experimental results for $[\text{Pu(IV)}]_{\text{aq}} > 10^{-8}$ M. Predictive simulations of Pu(IV) apparent solubility due to HA show that the chosen Pu(IV)-polymer has no impact for $\text{pH} > 4$. However, the comparison between these predictions and recent spectroscopic results suggest that more hydrolyzed polymeric Pu(IV) species can be stabilized by HA at $\text{pH} > 4$. Polymeric Pu(IV)-HA species might significantly enhance Pu(IV) apparent solubility due to humics, which support a colloid-facilitated transport of this low solubility element.

Keywords

Plutonium(IV), humic acid, complexation, polynuclear species, PHREEQC, Model VII.

1. INTRODUCTION

Humic colloids such as humic (HA) and fulvic (FA) acids are ubiquitous in natural waters and present a high binding capacity for dissolved metal ions. It has been evidenced that, in many cases, the mobility of metals in the environment was associated with colloidal transport (Kretzschmar et al., 2005). This is particularly the case for plutonium (Pu), a highly toxic and radioactive element. Significant amounts of Pu have been introduced into the environment by nuclear weapons tests, for instance. The aqueous chemistry of plutonium is rich and complex owing to its multitude of oxidation states ranging from +3 to +6 under environmental conditions. Among those, Pu(IV) exhibits the largest stability field and is considered as the most relevant oxidation state (Choppin, 2003). Although Pu(IV) was considered as rather immobile due to its extremely low solubility (approximately 10^{-11} - 10^{-10} M at pH=7; Neck and Kim, 2001), it shows a colloid-facilitated transport in presence of humic colloids. This behavior was shown in migration experiments of humic-rich ground water spiked with plutonium and other tetravalent metal ions like Th, Hf, and Zr (Artinger et al., 2003a, 2003b). Because of the strong interaction with humic colloids, the concentration of tetravalent trace metal ions in natural ground waters is directly related to the content of dissolved organic matter (DOC) (Artinger et al., 2003a). Because humic and fulvic acids are ubiquitous, they can play a significant role in the transport of plutonium to the biosphere wherever plutonium has been released: from final and intermediate repositories, by hazardous incident of nuclear power plants or facilities of the nuclear fuel cycle, or deposits from the atmosphere by atmospheric bomb tests and reentry of artificial satellites containing atomic batteries.

However, there are only a few experimental data about Pu(IV)-HA complexation that can be used for geochemical and transport modeling to assess the hazard of plutonium for the biosphere. Thanks to the very similar chemical properties of the f-elements, it is possible, for

a given redox state, to compare the stability constant with a ligand of different actinides (e.g. Th, U, Np, Pu). Reiller et al. (2008) reviewed all the available tetravalent actinide (An(IV)) complexation data with HA and found a high consistency between them. More recent Pu(IV)-HA binding studies are in relatively good agreement with the latter observation (Szabó et al., 2010; Sasaki et al., 2012). In these references, Pu(IV)-HA interaction is described in terms of complexation of mononuclear Pu with humic acid. However, a recent X-ray absorption spectroscopic (XAFS) study has yielded evidence for the formation of polynuclear Pu(IV) species with HA (Dardenne et al., 2009). This study suggested the formation of small polynuclear species (i.e. a few Pu atoms) rather than large-sized Pu(IV)-(hydr)oxide particles embedded in the organic matrix. Therefore, from the mechanistic point of view, it might be possible to consider these entities as polynuclear complexes with humic acid rather than precipitated nanophases stabilized in solution by organic polyelectrolytes.

An(IV) aquo ions have a high tendency to hydrolyse and to form amorphous hydroxide solids e.g. ($\text{PuO}_{2(\text{am,hyd})}$). In the presence of these amorphous solid Pu(IV)-(hydr)oxide, Pu(IV) can form eigen colloids (>1-2 nm) that can increase by two orders of magnitude the apparent solubility of plutonium (Neck et al., 2007). Furthermore, in acidic conditions, in the absence of solid (i.e. for solutions prepared below the saturation index of $\text{PuO}_{2(\text{am,hyd})}$) it has been shown that Th(IV) and Pu(IV) aqueous speciation is controlled by small polynuclear species (i.e. smaller than 1nm) (Walther et al., 2008, 2009). Contrary to Th(IV), where well-defined species could be identified (i.e. from dimers to hexamers), Pu simultaneously forms species of great variety. Therefore, on the one hand, intrinsic chemical properties of Pu(IV) might explain why polynuclear species are formed with HA. On the other hand, Pu(IV) eigen colloids might be stabilized by HA complexing groups. Indeed, it has been shown in the case of Np(IV) that small organic acids can stabilize polynuclear species (Takao et al., 2012), as well as in case of Pu(IV) with glycine (Knöpe and Soderholm, 2013). Earlier

studies have also observed the formation of polynuclear cation-HA species. In case of Al(III), Browne and Driscoll (1993) and Sutheimer and Cabaniss (1997) considered the formation of Al dimers to explain their complexation data. In case of Fe(III), there are spectroscopic evidences for the formation of Fe di- or trimers with HA (Gustafsson et al., 2007; Karlsson and Persson, 2010), although there are few complexation studies evidencing the formation of polynuclear cation-HA in batch experiment. It is interesting to note that trivalent Al and Fe present a high tendency to hydrolyze and to form polynuclear species in undersaturated solutions with respect to solid phases (e.g. Hellman et al., 2006; Sarpola et al., 2013), as it is the case for An(IV).

Although the stabilization of polynuclear Pu(IV)-HA species was suggested by spectroscopy and is mechanistically plausible, there is so far no quantification of such reactions in batch experiments. Indeed, previous studies aimed at investigating the interaction of mononuclear An(IV) with HA, and the formation of humic colloids consisting of small polynuclear metal species and HA was not considered. In contrast to all above mentioned studies, the present work aims at verifying the formation of polynuclear-Pu(IV)-HA species. The experiments were performed under acidic conditions in order to be able to study their interaction in a large range of final Pu(IV) aqueous concentrations by minimizing the formation of particulate Pu(IV)-(hydr)oxides or eigen colloids. A semi-mechanistical humic-ion binding model (Model VII: Tipping et al., 2011) was introduced into the geochemical speciation program PHREEQC (Parkhurst and Appelo, 1999) and was used as a tool to discuss the relevance of polynuclear-Pu(IV)-HA species and their potential impact on Pu(IV) apparent solubility due to HA complexation under acidic to neutral pH conditions.

2. MATERIALS AND METHODS

All chemicals were of pro analytical quality or better and were obtained from Merck (Darmstadt, Germany) or Riedel de Haen (Seelze, Germany). Milli-Q deionized water was used to prepare the solutions. The pH was measured by a pH meter (φ-310, Beckman, Germany) with a combined electrode (Beckman, Germany). The pH-meter was calibrated daily with certified commercial buffers at pH = 1, pH = 2, pH = 4, pH = 6 (Merck, Darmstadt, Germany).

2.1. Plutonium solution

For all the complexation studies, a 99.1 wt% ^{239}Pu stock solution (6.0×10^{-4} M), with small amounts of other isotopes (0.888 wt% ^{240}Pu , 0.014 wt% ^{241}Pu) and known specific activities was used. The plutonium solution was prepared by diluting an aliquot of the stock solution with 1 M HClO_4 . The solution then consisted of different oxidation states of plutonium. The tetravalent oxidation state of Pu was obtained by potentiostatic electrolysis in 1 M HClO_4 . For the electrolysis, a homemade glass electrolytic cell with three separated compartments (U-shape) was used. The middle one was used as a working electrode (Pt), the right one contained a Pt counter electrode and the left one contained the reference electrode (Ag/AgCl). These compartments were connected with a potentiostat for obtaining a constant potential at the working electrode. A mixture of Pu oxidation states was firstly electrolyzed at -0.6 Volt to obtain Pu(III), then Pu(IV) was fastly obtained from Pu(III) at 0.9 Volt. The purity of the Pu(IV) oxidation state was controlled by UV-Vis spectrometry (Cohen 1961). About 98 % of Pu(IV) and 2 % of Pu(IV) colloids were in the stock Pu solutions. The radioactivity concentration of ^{239}Pu was measured by liquid scintillation counting (LSC) using the scintillation cocktail Ultima Gold XR (Packard) and LSC Tricab (Hewlett Packard).

2.2. Humic acid (HA)

The commercially available Aldrich humic acid (AHA) (sodium salt, charge 37 no. 01816-054) was purified and isolated as described in (Kim and Buckau, 1988; Kim et al., 1990). The proton exchange capacity (PEC) is equal to $4.60 \times 10^{-3} \text{ eq g}^{-1}$ (Kim and Buckau, 1988; Kim et al., 1990; Seibert et al., 2001). Although AHA is sometimes criticized as a weak model for humic substances, its ion-binding behavior is rather similar to those of other humic substances (Avena et al., 1999; Milne et al., 2001, 2003; Saito et al., 2005; Pourret et al., 2007).

2.3. Complexation experiments

For the complexation experiments, HA and Pu(IV) were brought into contact at different pH values (1.8-3.0). The pH of the samples was adjusted by using a minimum of 0.1 M HClO₄ or 0.1 M NaOH solutions. The Pu(IV) concentration was $6.6 \times 10^{-8} \text{ M}$, and the humic acid content was varied between 0.01 and 25 mg/L and all mixtures were shaken continuously on an orbital shaker at 25°C. All experiments were performed at $I = 0.1 \text{ M NaClO}_4$ under aerobic condition at room temperature. Total sample volume was 10 mL in 20 mL vials. The samples were filtrated using ultrafiltration (1 kDa pore size) after 24 hours, 3 days, 1 week, and 2 weeks during preliminary complexation experiments. This preliminary study indicated that complexation equilibrium was established after 1 week, so 1 week for sampling was chosen in subsequent complexation experiments. The free Pu ion concentration was determined by liquid scintillation counting (LSC) of the filtrates. In absence of humic acid, the sorption of Pu(IV) on the filter material as well as on the vessel was determined and considered in the evaluations. In the case of humic acid, less than 5 % of HA passed through the 1kDa ultrafilter as measured by UV-Vis, which is being neglected in the present study. Pourret et al. (2007) also investigated AHA complexation properties using 5kDa ultrafilter

and also detected negligible amount of organic matter passing through the membrane by total organic carbon analysis. All experimental conditions and their results are given in the supporting information (Table S1).

2.4. Complexation modeling using PHREEQC and Model VII

The Humic Ion-Binding Model VII (Tipping et al., 2011) is an improved version of Model VI (Tipping, 1998). Both are based on the same equations but the total number of different cation binding sites required to describe HA heterogeneity is decreased in Model VII (= 50 versus 80 for Model VI). Model VI and VII are initially coupled with the inorganic speciation code WHAM. It is here coupled with PHREEQC (version 2) developed by Parkhurst and Appelo (1999), using the same strategy as used by Marsac et al. (2011) for Model VI. PHREEQC is a computer code based on an ion-association aqueous model, which was designed to perform speciation and saturation-index calculations in water. Thermodynamic constants are taken from NEA thermodynamic database (Guillaumont et al., 2003). Davies equation was used for activity coefficients calculation, being valid up to an ionic strength of 0.1 M.

A thorough description of Model VII can be found in Tipping et al. (1998; 2011). The model is a discrete binding site model which takes electrostatic interactions into account. Only the aqueous cation (e.g. Pu^{4+}) and its first hydrolysis products (e.g. PuOH^{3+}) are considered to bind to HA with the same binding constants. Eight sites are considered and divided into an equal number of type A sites (commonly associated with carboxylic functional groups) and type B sites (commonly associated with phenolic functional groups). There are n_A (mol g^{-1}) type A sites and $n_A/2$ type B sites. An average value for n_A ($3.3 \times 10^{-3} \text{ eq g}^{-1}$) was found by Tipping (1998) for various HA, leading to a PEC of $5.25 \times 10^{-3} \text{ eq g}^{-1}$, which is relatively similar to the Aldrich HA used here and was not modified. Proton binding is

described by the two median intrinsic protonation constants (pK_A or pK_B ; negative decadic logarithm of protonation constants K_A or K_B) and two parameters defining the spread of the protonation constants around the median (ΔpK_A or ΔpK_B). The intrinsic equilibrium constants for cation binding are defined by two median constants ($\log K_{MA}$ and $\log K_{MB}$), together with parameters (ΔLK_{1A} and ΔLK_{1B}) that define the spread of the values around the medians. However, satisfactory results are obtained by fixing $\Delta LK_{1A} = \Delta LK_{1B} = 0$. The work of Carbonaro and Di Toro (2007) showed that the relative binding strength of a metal cation with monodentate ligands is the same as those for protons. This concept was applied to carboxylic and phenolic HA groups in Model VII by Tipping et al. (2011). It is assumed that

$$\log K_{MB} = \log K_{MA} \cdot (pK_B/pK_A) \quad (1)$$

which reduces the number of adjustable parameters necessary to describe metal complexation by HA. A fraction of the type A and type B monodentate sites can form bi- (f_{bi}) and tridentate (f_{tri}) sites. The stability constants of these bi- and tridentate sites are defined by the sum of the $\log K$ values of the monodentate sites of which they are constituted. A small part of the stability constants of multidentate groups are increased by the ΔLK_2 parameter, the so-called "strong binding site term" (Tipping, 1998). In Model VII, ΔLK_2 is commonly attributed to the participation of additional HA ligands in the complex, such as the nitrogen-containing groups. However, Marsac et al. (2011) suggested that, in case of hard Lewis acids (e.g. trivalent lanthanides), a high ΔLK_2 value might be attributed to a chelation effect. ΔLK_2 is also the parameter of the HA site heterogeneity. An elevation of ΔLK_2 increases the range of the stability constants covered by the HA sites, thus increasing the heterogeneity of HA regarding cations binding.

An electrical double layer, where only counter-ions can accumulate, is defined. The double layer thickness is set by the Debye-Hückel parameter $\kappa = (3.29 \times 10^9 \times I^{1/2})^{-1}$ (Appelo and Postma, 2005), where I is the ionic strength (mol L^{-1}). The distribution of ions between

the diffuse layer and the bulk solution is calculated by a Donnan model. The electrostatic correction is represented by an empirical equation which mimics the Boltzmann factor:

$$\text{Exp} (-zF\psi/RT) = \exp (-2PzZ \log_{10}I) \quad (2)$$

where P is an adjustable parameter, z is the ion charge, Z is the net humic acid charge (eq g⁻¹), I is the ionic strength (mol L⁻¹), ψ is the surface potential (V), T is the temperature (K), F is the Faraday constant and R is the gas constant. In PHREEQC, the surface area (SA) is required:

$$SA = ZF \times (0.1174 \times I^{1/2} \times \sinh(F\psi/2RT))^{-1} \quad (3)$$

By combining eq.2 and eq.3, a relationship between SA and P is obtained. For I = 0.1 M, P = -196, whatever Z is valued, $|PZ \log_{10}I|$ becomes low and the sinh can be approximated by a linear function (Taylor's approximation). Indeed, R² = 0.996 is found when the sinh term versus Z is fitted with a linear function. The following equation is obtained:

$$SA = F \times (0.1174 \times I^{1/2} \times P \log_{10}I)^{-1} \quad (4)$$

which depends only on the ionic strength. We found SA~20000 m² g⁻¹ for I = 0.1 M. Although rather unrealistic, such high surface area is the consequence of translating the empirical electrostatic correction equation used in the initial version of Model VII into the double layer theory. Such high SA were also used in different studies, where Model V (Tipping and Hurley 1992) and VI were introduced into PHREEQC (Appelo and Postma, 2005; Liu et al., 2008; Marsac et al., 2011). To our knowledge there is no better solution at present. Note that the present approximation is only valid for any Z when both $|\log_{10} I|$ and $|P|$ are low. For lower I than 0.1 M or more negative P values (e.g. -330 as in Model VI), the linearization of the sinh function is only valid for a narrower range of Z values. It means that SA depends also on the pH. In this case, Marsac et al. (2011) simply chose a value of SA in PHREEQC/Model VI that fitted best the simulated HA proton titration simulated with

WHAM/Model VI, between pH 2 and 10. A summary of all Model VII parameters are given in the supporting information (Table S2).

As can be deduced from the latter description of Model VII, the description of HA binding properties is comparable with solid surface complexation modeling. Humic acid conformation changes with the physico-chemical conditions are not explicitly described. However, their impact on cation complexation might be included implicitly in the different binding parameters used. The physical state of the humic, i.e. probably coagulated for $\text{pH} < 2$ in the present study or even voluntarily insolubilized (Weber et al., 2006), is not supposed to impact the determination of cation-HA binding parameters for Model VII. It will be further illustrated in the present study.

2.5. Parameter estimation with PhreePlot

PhreePlot (Kinniburgh and Cooper, 2009) contains an embedded version of PHREEQC and is mainly used to produce certain types of high quality geochemical plots using PHREEQC such as pH-Eh diagrams, for instance. However, PhreePlot also includes a parameter optimization procedure, which fits automatically the model to the experimental data by minimizing the weighted sum of squares of the residuals. A modified Marquardt-Levenberg procedure (Powel, 1965) was applied, which provides incertitude on the estimated parameters. In the present study, PhreePlot was requested to fit $\log [\text{Pu}]_{\text{aq}}$ by optimizing $\log K_{\text{MA}}(\text{Pu(IV)})$, $\Delta\text{LK}_2(\text{Pu(IV)})$ as well as the formation constant of polynuclear Pu(IV) species with HA. Numeric tags can substitute numbers in the PHREEQC section of the PhreePlot input file. In Model VII, every Pu(IV)-HA complexation constants being calculated from $\log K_{\text{MA}}(\text{Pu(IV)})$ and $\Delta\text{LK}_2(\text{Pu(IV)})$, a readable form of Model VII must be written for PhreePlot using the keyword “numericTags” to make possible the automatic determination of optimizing $\log K_{\text{MA}}(\text{Pu(IV)})$ and $\Delta\text{LK}_2(\text{Pu(IV)})$ parameters.

3. RESULTS AND DISCUSSION

3.1. Plutonium(IV) interaction with humic acid

Fig. 1 shows the solubility of Pu(IV) as a function of pH calculated with PHREEQC from the following equation (Guillaumont et al., 2003):

The Pu(IV) concentrations at equilibrium ($[\text{Pu(IV)}]_{\text{aq}}$) in the present Pu-HA complexation experiments are below the solubility curve. Dotted lines represent the uncertainty on Pu(IV) solubility, as determined from the uncertainties of hydrolysis constants and solubility product. Therefore, no precipitation or Pu(IV)-colloids is expected. This statement might be, however, debatable at pH = 3 because here, $[\text{Pu(IV)}]_{\text{aq}}$ are higher than the minimum uncertainty limit of the Pu(IV) solubility.

Pu(IV)-HA complexation data were first treated as follows:

$$K_{\text{exp}} = \frac{[\text{Pu}_n\text{HA}]}{[\text{Pu}]_{\text{eq}}^n [\text{HA}]} = \frac{[\text{PuHA}] / n}{[\text{Pu}]_{\text{eq}}^n [\text{HA}]} \quad (7)$$

where K_{exp} is a conditional constant, $[\text{Pu}]_{\text{eq}}$ (in mol L^{-1}) and $[\text{PuHA}]$ (mol g^{-1} of HA) denotes the experimentally determined concentrations of Pu in the filtrate and in the retentate, respectively, and n is the stoichiometry of the reaction normalized to one HA site. $[\text{HA}]$ is defined here as the PEC (eq g^{-1}) of HA, i.e. the total site concentration, because it is not possible to determine precisely the free HA site concentration due to both HA site heterogeneity and the lack of knowledge about Pu(IV)-HA interaction. This implies that n and K_{exp} are only estimates of the stoichiometry and conditional formation constants of reaction 6. Applying some rearrangements to eq. 7, one obtains a Freundlich-type isotherm equation:

$$\log \frac{[\text{PuHA}]}{[\text{HA}]} = \log K_{\text{exp}} + \log n + n \log [\text{Pu}]_{\text{eq}} \quad (8)$$

Fig. 2 presents the amount of Pu(IV) complexed to HA (in mol eq⁻¹) as a function of Pu(IV) equilibrium concentration ([Pu(IV)]_{eq}), i.e. the Pu(IV)-HA binding isotherm. The concentration of plutonium humic complexes (Pu(IV)-HA) increases with pH due to the decrease of proton competition for HA binding groups in the complexation reaction. From low (10⁻⁹ M) to intermediate Pu concentrations (10⁻⁸ M, [Pu(IV)]_{eq}), the slope of the log-log isotherm is with a value of 0.73 significantly below 1 (illustrated for pH 3 in Fig. 2). This is explained with the heterogeneity of HA sites for Pu(IV) complexation. The latter pH and metal loading effects have been widely described for many cations complexation by humic substances, and a slope below 1 is commonly observed for cations binding to humic even at low site occupancy (e.g. Benedetti et al., 1995). However, for [Pu(IV)]_{aq} > 10⁻⁸ M, the mean slope of the isotherm of all pH values drastically increases to a value of 3.5 (3.8 as illustrated at pH = 3; Fig. 2). At pH = 3, this observation might be firstly attributed to the precipitation of Pu(IV)-(hydr)oxides or at least to formation of Pu(IV) eigencolloids because experimental [Pu(IV)]_{aq} values are near to the Pu(IV) solubility limit. However, the same high slope (3.94) is observed at a more acidic pH value of 1.8, where it is clear that Pu(IV) does not precipitate in the range of [Pu(IV)]_{aq} studied here. It is well established that Pu(IV) is the most stable Pu redox state in the presence of HA even under anaerobic conditions (Marquardt et al., 2004; Dardenne et al., 2009). Furthermore, the present experiments were performed in contact with air preventing the formation of Pu(III). Therefore, the slope of the isotherm being larger than 1 is not a result of oxidation state transformation during the experiment, but might be attributed to the presence of Pu(IV) polynuclear species. Because Pu(IV) solubility was determined by ultrafiltration at 3 kDa (pore size: 1-2 nm; Neck and Kim, 2001) to separate Pu(IV)-HA complexes from the solution, the increase of the amount of Pu(IV) in the HA fraction of our experiments can only be attributed to polynuclear Pu(IV) species associated to the HA colloids. Indeed, earlier studies showed no significant difference between 3 kDa and 1

kDa ultrafilter for the separation of Pu(IV)-HA complexes. If we consider a linear binding behavior of polynuclear Pu(IV) species to HA, the slope of the isotherm equal to 3.5 suggests the formation of 3:1 or 4:1 Pu-HA complexes, presuming a polynuclear Pu(IV) species binds to one HA site. When considering the 4:1 stoichiometry, at pH=3, a condition constant of $\log K_{\text{exp}}=27.3$ can be estimated for the humate complexation reaction (6). However, due to HA heterogeneity, binding of polynuclear Pu(IV) species to HA might not be linear, and would imply a higher degree of Pu(IV) polynucleation. This stoichiometry is actually more likely an average value because a large variety of polynuclear species might be formed at the same time with HA, as it has been observed by Walther et al. (2009), in solution under similar conditions, but below the solubility limit.

3.2. Modeling with PHREEQC/model VII

The preceding interpretations are tested with the humic-ion binding model, Model VII. Phreeplot was used to calibrate Pu-HA binding parameters in Model VII fitting the present experimental data. This automatic fitting procedure also provides the uncertainty of the determined parameters. The optimized model parameters are presented in Table 1 and are compared with the estimated values determined by Stockdale et al. (2011) that were used here as initial values for the fit. $\log K_{\text{MA}}$ (i.e. the main binding parameter) and ΔLK_2 (i.e. the strong sites binding parameter) were found equal to 3.9 ± 0.2 and 1.7 ± 0.5 , respectively. These results are not significantly different from the estimated values of Stockdale et al. (2011) and validate the estimation method. For Th(IV), Tipping et al. (2011) have determined $\log K_{\text{MA}}(\text{Th(IV)}) = 3.58$ and $\Delta\text{LK}_2(\text{Th(IV)}) = 0.23$, which are slightly lower than the presently determined values for Pu(IV). But when applying the uncertainties from the Pu(IV) fit on the Th(IV) values, both data set can be regarded as very similar within the range of uncertainties. The simulated results are also illustrated as binding isotherms in Fig. 3 (dotted lines), when

considering only the binding of Pu(IV)-monomers to HA. The model can reproduce relatively well the results for $[Pu(IV)]_{aq}$ below approximately 10^{-8} M. Obviously, the model cannot reproduce the change in the slope of the binding isotherm at $[Pu(IV)]_{aq}$ higher than 10^{-8} M, for the reasons explained before.

The reaction of polynuclear An(IV) species stabilization by carboxylic ligands was written as follows by Takao et al. (2012):

$$K_{poly} = \frac{[(RCOO)_a An_b O_c H_d][H^+]^{(c+d)}}{[RCOO^-]^a [An^{4+}]^b} \quad (10)$$

where a, b, c, and d are, respectively, equal to 12, 6, 8 and 4 in case of formate (R = H, log $K_{poly} = 42.7$ at I = 0.62 M) and acetate (R = CH₃, log $K_{poly} = 52.0$ at I = 0.66M), for An = Np. In case of Pu(IV)-HA complexation, the stoichiometry seems to be approximately 4:1, according to the present experiments. The pH dependence of the reaction is, however, very difficult to evaluate because of HA site heterogeneity, the competition between Pu(IV) and H⁺ for these sites and the hydrolysis of Pu(IV) formed with HA. Furthermore, Walther et al. (2009) observed a large variety of the number of Pu atoms in the polynuclear species. As mentioned before, the stabilization of polynuclear Pu(IV) species by HA should probably be described by a distribution of polynuclear Pu(IV) species. Unfortunately, it appears not possible for the moment to provide a more precise description of the formation of polynuclear Pu-HA species by modeling, because the distribution of the polynuclear species is unknown. The modeling exercise in the present paper is based on several assumptions. Although it can be regarded as a rough estimation of this complex system, it will help us as an illustration to discuss the relevance of such polynuclear species under environmental conditions. Because $Pu(OH)_2^{2+}$ is the dominant species in solution (see Fig. S1) from which polynuclear compounds are formed via edge sharing, the formation reaction of tetra-Pu(IV)-HA complexes was introduced in Model VII as follows:

Only the mono-carboxylic sites defined in Model VII were considered, which represent 43.5% of the total HA carboxylic groups because the fraction of bi- and tridentate sites is fixed. Indeed, the 4:1 stoichiometry of the complexes would not have been respected when considering the complexation of Pu-tetramer to bi- and tridentate HA sites as defined in Model VII. The logarithm of the formation constant of reaction (11) was found to be 31.4 ± 0.4 . This value is higher than the conditional formation constant estimated by the slope analysis (e.g. 27.3 at pH = 3; Fig. 2) because, (i) the latter one did not take into account the HA sites occupancy by Pu and protons, and (ii) only 43.5% of HA sites are involved according to Model VII definition of monodentate sites. Although this tetramer complex presents a high positive charge, it might be compensated by the overall HA negative charge. The complexation of relatively highly charged polynuclear species to humics are generally required to model data obtained in acidic condition: $\text{Al}_2(\text{OH})_4^{4+}$ (Sutheimer and Cabaniss, 1997), Fe_2O^{4+} (Gustafsson et al., 2007) or $\text{Fe}_3\text{O}_2^{5+}$ (Marsac et al., 2013). Note that in the present model, the Pu-tetramer-HA formation reaction suggests HA sites as templates for bridge bonding between hydroxy-Pu(IV) ions, which is consistent with the previous trivalent cation-humics studies. The results of the fit are presented in Fig. 3. The model can reproduce the data at pH 1.8 relatively well whereas more deviations are observed at pH 3. By increasing the pH, the distribution of hydrolyzed polymeric An(IV) species increases (Walther et al., 2009). The deviation observed at pH = 3 might be a direct consequence of the strong simplification of the system in the model by introducing only one type of polynuclear Pu(IV) species. Nevertheless, considering such (over)simplification, this approach can reproduce the experimental results relatively well.

3.3. Comparison with An(IV)-HA binding data from literature

Reiller et al. (2008) compiled and re-interpreted the An(IV)-HA (An = Th, U, Pu) complexation data available in the literature. They recalculated conditional complexation constants as follows:

$${}^{\text{HA}}\beta(\text{An}^{4+}) = \frac{[\text{AnHA}]}{[\text{An}^{4+}]_{\text{aq}}[\text{HA}]} \quad (13)$$

where [HA] is calculated from the proton exchange capacity (eq g⁻¹). The concentration of the An⁴⁺ aquo cation [An⁴⁺]_{aq} are very low and are calculated from the total aqueous An(IV) concentration ([An(IV)]_{aq}) measured experimentally and the hydrolysis constants (β_{1,n}) of the considered An(IV):

$$[\text{An}^{4+}]_{\text{aq}} = [\text{An(IV)}]_{\text{aq}} \times \left(1 + \sum_{n=1}^4 \frac{\beta_{1,n}}{[\text{H}^+]^n} \right) = [\text{An(IV)}]_{\text{aq}} \alpha_{\text{An}} \quad (14)$$

The site reaction coefficient α_{An} considers all hydrolysis reactions of the An⁴⁺ cation. They found a high consistency between all tetravalent actinides by only using the hydrolysis constants of U(IV) for all An(IV) hydrolysis reactions and they derived the following equation:

$$\log {}^{\text{HA}}\beta(\text{An}^{4+}) = (3.26 \pm 0.10)\text{pH} + (0.14 \pm 0.67). \quad (15)$$

The present experimental results were recalculated with the approach of Reiller et al. for [Pu(IV)]_{aq} < 10⁻⁸ M (i.e. where Pu(IV) binds to HA as monomeric species) and are plotted in Fig. 4 as well as the results of eq. (15) (Reiller et al., 2008) for different pH. The consistency between the present log ^{HA}β(Pu⁴⁺) data for [Pu(IV)]_{aq} < 10⁻⁸ M and eq. 15 shows that our results are in excellent agreement with literature. In at least part of our experiments (i.e. for pH < 2), HA has coagulated. This result suggests that the physical state of the humic has no significant impact on its binding properties, which was already observed in earlier studies for An(III) or Fe(III) (Kim et al., 1993; Weber et al., 2006). Note that because of the

low solubility of An(IV), experiments performed at high pH had low $[\text{An(IV)}]_{\text{tot}}$. Therefore, the slope of eq. (15) takes also into account, implicitly, the effect of low metal loading of HA.

Simulations with PHREEQC/Model VII were performed as a function of the pH using 10 mg/L of HA and $[\text{Pu(IV)}]_{\text{tot}}$ 10 times below the solubility limit. Such conditions are commonly investigated to avoid $\text{An(OH)}_{4(\text{am})}$ precipitation or colloid formation in the sample. The contribution of Pu(IV) tetramer is also negligible. The results of the simulations were recalculated according to eq. (13) – (14) and taking into account the default PEC value of HA in Model VII. These results are illustrated together with the results according to eq. (15) (Reiller et al., 2008) in Fig. 4. Although Pu(IV)-HA binding parameters in Model VII were calibrated only with our experimental results obtained under acidic conditions (i.e. $\text{pH} \leq 3$), the evolution of $\log {}^{\text{HA}}\beta(\text{Pu}^{4+})$ with pH is well described up to $\text{pH}=7$, attributing to Model VII some efficiency as a predictive tool. The uncertainty of Model VII parameters presently determined (bold dotted lines) are comparable with the uncertainty of $\log {}^{\text{HA}}\beta(\text{An}^{4+})$ determined by Reiller et al. (2008). As mentioned earlier, only the binding of Pu^{4+} and PuOH^{3+} to HA were considered. This finding is opposed to the Charge Neutralization Model (CNM), commonly used to describe actinides complexation by humic acids (Kim and Czerwinski, 1996). This model requires the binding of several hydrolysis products of Pu(IV) to HA to simulate the pH dependence of $\log {}^{\text{HA}}\beta(\text{Pu}^{4+})$. However, the CNM does not take into account the heterogeneity of HA and cannot reproduce the effect of the metal loading, for instance. Model VII considers the presence of strong chelating sites in low amount. Due to the low solubility of $\text{PuO}_{2(\text{am,hyd})}$, $[\text{Pu(IV)}]_{\text{aq}}$ becomes very low under near neutral conditions. Therefore, in such conditions, Pu(IV) is considered to be complexed by chelating sites of HA. It has been shown that chelating ligands can inhibit An(IV) hydrolysis (e.g. Jeanson et al., 2010) even under alkaline conditions. The description of Pu(IV)-HA interaction provided by Model VII might be considered as relatively consistent from the mechanistic point of view.

Model VII underestimates $\log {}^{\text{HA}}\beta(\text{Pu}^{4+})$ for $\text{pH}>7$, suggesting that more hydrolyzed Pu(IV) species, such as $\text{Pu}(\text{OH})_2^{2+}$, might have to be considered as species bound to HA. However, preliminary tests (not presented here) showed that $\text{Pu}(\text{OH})_2^{2+}$ Model VII parameters had to be optimized independently from PuOH^{3+} , which lead to an increase in the number of adjustable parameters. Furthermore, a binding isotherm up to high loading cannot be obtained experimentally for $\text{pH}>7$ because of the low solubility of $\text{PuO}_{2(\text{am,hyd})}$. Therefore, it is not possible to constrain $\text{Log } K_{\text{MA}}$ and ΔLK_2 for $\text{Pu}(\text{OH})_2^{2+}$ independently. Predictive modeling of Pu(IV) solubility in the presence of HA would give very different results depending on the choice of the couple $\text{Log } K_{\text{MA}}/\Delta\text{LK}_2$. Furthermore, it does not seem very clear if additional parameters (i.e. the complexation of more hydrolyzed Pu(IV) monomers) have to be considered in the calculations. Indeed, cation complexation constants with HA multidentate sites in Model VII are subjected to a large uncertainty. For instance, the uncertainty associated with the formation of a bidentate complex is twice the sum of the corresponding monodentate ones. The strong sites are additionally subjected to the incertitude associated to ΔLK_2 . This can somewhat be seen, for instance on figure 4: at low pH, the simulation was performed at higher $[\text{Pu(IV)}]_{\text{tot}}$ than at high pH. Therefore, at low pH, the incertitude on $\log {}^{\text{HA}}\beta(\text{Pu}^{4+})$ is almost not visible on figure 4 because Pu(IV) speciation with HA is dominated by lower denticity sites than at higher pH, where the strong HA multidentate sites are dominant. A slight modification of already existing parameters describing the strong sites in Model VII might improve significantly the simulation for An(IV) complexation to HA without considering additional parameters. However, the present study does not aim at revising Model VII. Therefore, the present discussion will be limited to $\text{pH}<7$, where only the complexation of Pu^{4+} and PuOH^{3+} binding to HA can reproduce relatively well the experimental results.

3.4. Relevance of poly-Pu(IV)-HA species under circumneutral conditions

Dardenne et al. (2009) have studied the Pu(IV)-HA formation by XAFS in a humic-rich groundwater ($\sim 70 \text{ mgC L}^{-1}$) at $\text{pH} \sim 7$ and a Pu concentration of $1.4 \times 10^{-4} \text{ M}$. In presence of HA, this Pu(IV) concentration is approximately 10^6 times higher than Pu(IV) solubility limit in 0.1 M NaCl aqueous solution at $\text{pH} = 7$. In the experiment, a precipitation of potential Pu(IV)-(hydr)oxide was not observed and the good quality of the data confirms that a significant fraction of the Pu(IV) remained in solution. Indeed, to be able to record an Extended X-ray Absorption Fine Structure (EXAFS) spectrum up to $k = 11 \text{ \AA}^{-1}$, Pu(IV) concentrations of $\sim 100 \text{ ppm}$ are typically required in the solution, which corresponds to $\sim 10^{-4} \text{ M}$ of Pu(IV). The EXAFS showed a significant Pu-Pu signal. Furthermore, the Pu L3-edge XANES (X-ray Absorption Near Edge Structure) was very similar to aqueous Pu(IV) (i.e. in a solution at $\text{pH} = 0$) and differed strongly from solid $\text{PuO}_{2(\text{am,hyd})}$ or from colloidal Pu(IV) in solution (Walther et al., 2009). From the mechanistic point of view, it might be possible to consider these entities as polynuclear complexes with humic rather than precipitated nanophases. In neutral to alkaline pH conditions, when the solution is in contact with solid $\text{PuO}_{2(\text{am,hyd})}$, the formation of Pu(IV) eigencolloids can only increase Pu(IV) apparent solubility up to $10^{-8.3 \pm 0.5} \text{ M}$ (Neck et al., 2007). These results evidenced that natural organic matter can inhibit the precipitation of $\text{PuO}_{2(\text{am,hyd})}$ by the formation of small polynuclear Pu(IV) humate species. Although there is no available systematic solubility study of Pu(IV) in the presence of HA, the large amount of Pu remaining in solution in the experiments of Dardenne et al. (2009) suggests also that HA can enhance Pu apparent solubility. This might also impact Pu mobility in organic-rich environments, provided that a significant amount of Pu-HA does not aggregate.

The Pu(IV) apparent solubility in presence of HA was simulated with PHREEQC/Model VII for $2 < \text{pH} < 7$, i.e. in a range of pH conditions where Model VII gave

satisfactory results, in a 0.1 M NaCl solution containing 140 mg L⁻¹ of HA. This [HA] corresponds to 70 mg L⁻¹ of dissolved organic carbon (DOC), considering that carbon represents 50 wt.% of HA. These conditions reproduce roughly the Gorleben groundwater (Marquardt et al., 2004) and they were investigated here as an illustration rather than in sense of a prediction. Aqueous Pu(IV) and Pu(IV)-HA species were considered as dissolved species. Results are presented in Fig. 5. When considering only the formation of monomeric Pu(IV)-HA species, HA can significantly enhance Pu(IV) apparent solubility for pH>2.5. At pH=7, the apparent solubility in presence of HA is underestimated by more than 3 orders of magnitude, compared with the sample studied by XAFS by Dardenne et al. (2009). Note also that the precipitation of metallic (hydr)oxides in the presence of HA might lead to highly amorphous or nanometric (hydr)oxides with an enhanced solubility. This was the case, for instance, for Fe(III) whose (hydr)oxides formed in the presence of HA had a higher solubility than ferrihydrite, an amorphous Fe(III)-hydroxide (Weber et al., 2006; Marsac et al., 2013). However, the increase of Fe(III) solubility in presence of HA did not exceed one order of magnitude. When considering additionally the formation of polynuclear Pu(IV)-HA species, Pu(IV) apparent solubility increases in presence of HA by 1.5 log units at pH=3. The arbitrarily chosen Pu(IV) tetramer to illustrate the present experimental results between pH 1 and 3 has no impact for pH > 4 and cannot explain the XAFS results of Dardenne et al. (2009). Actually, the fact that the Pu(IV) tetramer has only an impact in conditions quite similar to the present experiments is rather comforting because its occurrence at pH > 5 would have been highly questionable. Nevertheless, these simulations show that the stabilization of a more hydrolyzed Pu_n(OH)_m species than Pu₄(OH)₈⁸⁺ by HA should be considered in the model to produce simulations consistent with spectroscopy.

To our best knowledge, the only experimental An(IV) solubility data in the presence of organic matter were performed with U(IV) in the presence of carbonates (Cachoir et al.,

2003; Delécaut et al., 2004). Such data are relevant for performance assessment of nuclear waste disposal but it is difficult to determine precisely which chemical mechanisms hide behind the observed behavior. Under these conditions, U(IV) can easily be oxidized to U(VI) and carbonates can compete with organic matter. Indeed, Reiller et al. (2008) analyzed the data by geochemical speciation modeling and discussed the factors that could have an influence on uranium concentration in the HA-containing solution. The finally presented simulated results, although very promising, still underestimated U solubility data. However, the stabilization of polynuclear U(IV)-HA species could not be tested because there was no clear evidence of such species in the literature. By comparison with the present results for Pu(IV), the formation of polynuclear actinide(IV)-HA might be an alternative explanation for the deviation observed between experimental and modeling results. However, it is very difficult to estimate precisely the thermodynamic parameters of such reaction yet, especially under near neutral pH conditions.

4. CONCLUSION

The present study on Pu(IV) humate complexation at $\text{pH} < 3$ yields evidence for the complexation of both mono- and polynuclear Pu(IV) species to HA, at conditions where no Pu(IV) precipitation is expected. Model VII is used to simulate Pu(IV) monomers binding to HA. The simulations are consistent with other tetravalent actinides-HA binding data from literature (Reiller et al., 2008). The stabilization of a Pu tetramer ($\text{Pu}_4(\text{OH})_8^{8+}$) by HA is proposed to illustrate Pu(IV)-HA interaction in conditions where polynuclear Pu(IV)-HA species are formed. Although a robust model considering both the formation of mono- and polynuclear Pu(IV) complexes with HA cannot be derived from the present and previous studies, such polynuclear species are expected to have an impact under relevant conditions in the environment. They significantly increase the Pu(IV) apparent solubility due to HA

complexation, more than by humate complexation of monomeric Pu(IV) species. Due to their similar chemical properties, comparable mechanisms are also expected for other tetravalent actinides, such as U(VI) and Np(IV). Such a mechanism of humate or fulvate complexation strongly supports a transport of An(IV) as a humic colloid-borne species as observed in migration experiments (Artinger et al., 2003a,b). Therefore, further studies should be dedicated to the colloidal stability of An(IV)-HA (i.e. mono- and polynuclear) complexes. More generally, the stabilization of polynuclear cations by HA seems to be a relevant mechanisms at least for cations presenting a high tendency for hydrolysis such as An(IV), Al(III) (Browne and Driscoll, 1993; Sutheimer and Cabaniss, 1997) or Fe(III) (Gustafsson et al., 2007; Karlsson and Persson, 2010). This might impact on the fate of these elements in the environment but might also affect other elements through the competition for organic matter binding sites.

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Table and Figure caption

Table 1. Pu(IV)-HA binding parameters in Model VII ($\log K_{MA}$ and ΔLK_2) presently determined. Estimated values by Stockdale et al. (2011) and fitted parameters for Th(IV)-HA complexation (Tipping et al., 2011) are also shown for comparison.

Figure 1. Comparison between Pu(IV) concentration determined experimentally at equilibrium in the presence of HA at pH=1.8, 2.5 and 3 ($[Pu]_{tot} \sim 6 \cdot 10^{-8} M$, $0.025 < [HA] < 25 \text{ mg L}^{-1}$) and Pu(IV) solubility limit calculated from Pu(IV) hydrolysis and solubility product given in Guillaumont et al. (2003) (plain line) with the corresponding incertitude (dashed lines), in 0.1M of $NaClO_4$.

Figure 2. Pu(IV) binding to HA as function of $\log [Pu(IV)]_{aq}$ at pH 1.8, 2.5 and 3. A "break" in the binding isotherm is observed and is illustrated at pH 3 by fitting the data with two linear functions, $[HA] = 0.025\text{-}25 \text{ mg/L}$, $I = 0.1M \text{ NaClO}_4$, contact time = 1 week, Ultrafiltration (1kDa).

Figure 3. Comparison between experimental and modeling results of Pu(IV)-HA binding considering or not the stabilization of Pu(IV) tetramer by HA.

Figure 4. Evolution An^{4+} -HA conditional stability constant versus pH as calculated from eq. 15 (Reiller et al. 2008; solid line within the incertitude presented as dashed lines). The present experimental data (grey squares) and simulated results with Model VII (bold line) are also presented for comparison, associated with the incertitude on Model VII parameters (bold dotted lines).

Figure 5. Simulated Pu(IV) solubility versus pH in a 0.1M of NaCl solution containing 140 mg L^{-1} of HA or no HA. The experimental condition studied by XAFS (Dardenne et al., 2009), where polynuclear Pu(IV)-HA species were evidenced, is also shown for comparison.

	Pu(IV) (present study)	Pu(IV) (estimated)	Th(IV)
Log K _{MA}	3.9±0.2	4.08	3.58
ΔLK ₂	1.7±0.5	1.85	0.23

Table 1

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5