

## Prognosticating the humic complexation for redox sensitive actinides through analogy, using the charge neutralisation model.

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### Abstract

The complexation of redox sensitive elements by humic acid (HA), described through the charge neutralisation model (CNM) has been reviewed in order to have a comprehensive scope. The data acquired in HUMICS program on thorium (IV), and data available in the literature, were reinterpreted according to the CNM, and adapted to uranium (IV), neptunium (IV) and plutonium (IV) through analogy in order to draw a boundary prediction. Otherwise, available data obtained in the framework of the CNM were used, or adapted if necessary, for other redox states when the analogy is justified, *i.e.*  $\text{Am}^{3+}$ - $\text{Cm}^{3+}$  for  $\text{Pu}^{3+}$ ,  $\text{NpO}_2^+$  for  $\text{PuO}_2^+$  and  $\text{UO}_2^{2+}$  for  $\text{PuO}_2^{2+}$ .

The obtained speciation diagrams indicate that, when (HA) = 100 mg/L, redox sensitive actinides should be reduced to their +IV state when  $E_H \leq 650$  mV/SHE for plutonium,  $E_H \leq 100$  mV/SHE for neptunium and  $E_H \leq -20$  mV/SHE for U. Plutonium could be present as mixtures of plutonium (III) and (IV) depending on the pH value in reducing ground waters  $-150 \leq E_H$  (mV/SHE)  $\leq 150$ . The known reduction of neptunium (V) to neptunium (IV) in Gorleben ground waters seems also well represented, so does the stability of uranium (VI) in humic solution when  $E_H \geq 100$  mV/SHE. Conversely, the known association of plutonium (VI) in marine systems are not satisfactorily represented, so does is the uranium behaviour under reducing conditions. Experiments under well-controlled conditions are still needed to ascertain the plutonium and uranium compartment in the presence of humic acid.

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## 1. Introduction

The aqueous chemistry of actinide elements is one of the most intricate and interesting chapters of the general chemistry of these elements. In particular, uranium, neptunium and plutonium are redox sensitive in aqueous solutions, and the study of their complexation properties has been a challenging puzzle for generations of scientists. As the reduced states are difficult to stabilise in solution, there is a large discrepancy between the different published values of complexation constants. Therefore, the use of analogies is a convenient way to estimate unknown complexation constants [1], knowing the limitation of the approach [2].

The complexation of actinides by humic substances (HS), which represent about 40-60 % of the natural organic matter (NOM), is not an exception. Humic substances are the alkaline extracted fraction of the NOM. From this primary fraction are extracted three sub-fraction namely: humine that is insoluble at whatever pH; humic acids (HA) that are not retained on a hydrophobic resin and insoluble at acidic pH; fulvic acids (FA) that are retained on a hydrophobic resin and are soluble at whatever pH.

A lot of works have been undertaken on “stable” redox states, *i.e.* uranium (VI), neptunium (V) and americium/curium/europium (III). Experimental difficulties have often prevented from obtaining reliable results on reduced states of uranium, neptunium or plutonium. Furthermore, the redox properties of humic substances [3-5] have led to confusing results for protactinium [6], neptunium [7, 8], plutonium [9-12] and other elements [13-19], even if the use of ligands to stabilise redox state is well known in the nuclear industry [20-23]. Otherwise, the reduction of uranium (VI) by HS has not been clearly observed up to now [24-26].

The complexation of metals by humic substances has been a subject of extensive works in the past decades. The main problem concerning thermodynamic descriptions of humic complexation is the apparent increasing complexation strength with pH. This phenomenon is related to the increasing ionisation of functional groups (“carboxylic” and “phenolic”) with increasing pH. This increasing complexation strength was modelled using either global varying complexation coefficients [25, 27],<sup>1</sup> varying number of sites [28], multi-pKa approaches [29], and statistical description [30-32]. The latter type of model could be seen as more representative of the aggregate structure of HS [33, 34], and could account for competition with other metals more accurately [31, 32, 35]. Nevertheless, the more operational type of description has been widely applied to actinides and a large number of data are available in literature.

The charge neutralisation model (CNM) [28] has been applied to a lot of relevant actinides namely uranium (VI) [24, 36], neptunium (V) [37-39], americium, curium and

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<sup>1</sup> This implies that the “constants” are not “real” thermodynamic constants.

europium (III) [40-43]. The variation of the number of available sites can be seen as a continuous term. Only few attempts have been reported up to now in the intricate cases of actinides (IV) and plutonium [44]. Even if the strong interaction of actinide (IV) with HS is known [36, 45-49], the available data on humic complexation are scarce. Nash and Choppin, more than twenty years ago in the framework of a polyelectrolytic model,<sup>2</sup> obtained high interaction parameters for thorium (IV) between pH 3.9 and 5 for different humic and fulvic acids [50]. Recently, data has been obtained under neutral pH conditions [44, 51].

The interactions with neptunium and plutonium are more confusing as HS induce redox reactions [6, 9-11]. Nevertheless, the complexing properties of HS towards almost all of the redox analogues of these elements have received great attention.

The aim of this exercise is to reinterpret and adapt the available data in the literature in the framework of the CNM in order to define the scope of humic complexation of redox sensitive elements.

## 2. Treatment of data

Only the complexing properties of HS will be considered here, since their reducing properties have not totally been clarified.

### 2.1. CNM model

The description of the CNM has been done elsewhere and will not be completely developed here [28]. Through this model, the increasing complexation strength with pH is managed through a varying parameter LC, the loading capacity, which represents the maximum fraction of the humic sites  $[HA(z)]_T$  involved in a complexation reaction. Hence the complexation is described by a “real constant”.



where  $[HA(z)]_F$  and  $[M^{z+}]_F$  are respectively the concentrations of free humic sites and  $M^{z+}$  in solution. The total concentration of humic sites available to complex and neutralise a metal ion  $M^{z+}$  is written as:

$$[HA(z)]_T \text{ (eq/l)} = \frac{(HA) \text{ (g/L)} \times \text{PEC (eq/g)}}{z} \quad (2),$$

where (HA) is the concentration of HA in g/L, PEC is the proton exchange capacity (eq/g) determined by titration.

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<sup>2</sup> Using increasing complexation coefficient with pH.

The free humic site concentration  $[\text{HA}(z)]_F$  is defined as the difference between the maximum concentration of humic sites available for the metal  $\text{LC} \times [\text{HA}(z)]_T$ , and the actual concentration of humic sites that are involved in the complexation  $[\text{MHA}(z)]$ .

$$[\text{HA}(z)]_F = \text{LC} \times [\text{HA}(z)]_T - [\text{MHA}(z)] \quad (3)$$

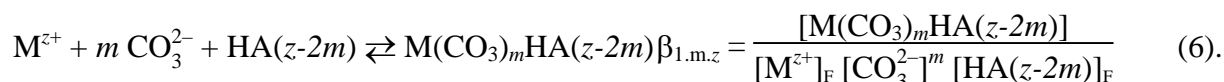
The complexation constant is thus written as:

$$\beta_{1,z} = \frac{[\text{MHA}(z)]}{[\text{M}^{z+}]_F \left( \text{LC} \times [\text{HA}(z)]_T - [\text{MHA}(z)] \right)} \quad (4)$$

Nevertheless, in the case of moderately hydrolysed actinides (*e.g.*  $\text{Am}^{3+}$  or  $\text{UO}_2^{2+}$ ), the authors have managed the metal-HA interaction increase with pH by postulating the formation of mixed complexes [52-54]:



Panak *et al.* [52] have also noticed spectroscopic modifications of Cm(III) in the presence of HA with increasing pH and carbonate concentration. They postulated the occurrence of mixed carbonato species through the reaction:



In these cases, LC is not easy to determine and the authors postulated that  $\text{LC} \equiv 1$  due to the pH value close to the total ionisation of the HS ( $\text{pH} \geq 6$ ) [52, 53].

## 2.2. Reinterpretation of thorium (IV) literature data through CNM

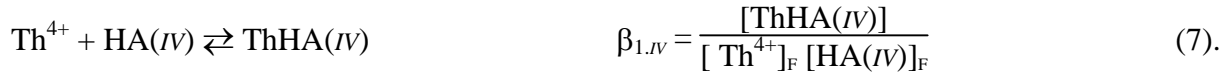
### 2.2.1. Formation of ThHA(IV)

The hydrolysis and carbonatation of thorium (IV) in solution is still a matter of debate [55-61]. Nevertheless, it is commonly accepted that  $\text{Th}^{4+}$  is less prone to hydrolysis than other actinides (IV). The humic complexation<sup>3</sup> of thorium (IV) in acidic media has been studied by Nash and Choppin [50] using liquid-liquid extraction from water.<sup>4</sup> From the complexation constants available in [50] taken from [55, 62], it can be calculated that the chemistry of thorium (IV) is dominated by acetate complexation.

The reaction between  $\text{Th}^{4+}$  and HA(IV) can be written:

<sup>3</sup> Humic acid from Lac Bradford

<sup>4</sup> Sodium acetate 0.05 M - sodium perchlorate 0.05 M in toluene with di-2-ethylhexyl phosphoric acid



The available data can be used to calculate  $\log \beta_{1,\text{IV}}$ . Using the Schubert formalism [63, 64], and under the conditions that thorium is present at trace concentration, and when no HA are present, the distribution coefficient of thorium between organic and aqueous phase is written as:

$$D^{\circ} = \frac{[\text{Th}]_{\text{org}}}{[\text{Th}]_{\text{aq}}} \equiv \frac{[\text{Th}]_{\text{org}}}{[\text{Th}^{4+}] \times \left( 1 + \sum_{i=1}^n \frac{* \beta_i}{[\text{H}^+]^i} + \sum_{j=1}^m \beta_j^{\text{AcO}} \left( \frac{[\text{AcOH}]_{\text{T}}}{1 + \beta^{\text{H}} [\text{H}^+]} \right)^j \right)} = \frac{[\text{Th}]_{\text{org}}}{[\text{Th}^{4+}] \times \alpha} \quad (8).$$

where  $*\beta_i$  are the thorium (IV) cumulative hydrolysis constants,  $\beta_j^{\text{AcO}}$  are the cumulative constants for acetate complexation,  $\beta^{\text{H}}$  is the protonation constant for acetate ion and  $\alpha$  is the complexation coefficient.

Assuming that humic complexes are not extracted in the organic phase, the distribution coefficient is thus written:

$$D \equiv \frac{[\text{Th}]_{\text{org}}}{[\text{Th}^{4+}] (\alpha + \beta_{1,\text{IV}} [\text{HA}(\text{IV})]_{\text{F}})} \quad (9)$$

From equation (8) and (9), comes the expression of  $\beta_{1,\text{IV}}$ :

$$\beta_{1,\text{IV}} = \left( \frac{D^{\circ}}{D} - 1 \right) \frac{\alpha}{[\text{HA}(\text{IV})]_{\text{F}}} \quad (10).$$

Knowing that  $^{230}\text{Th}$  is used as a tracer, the balance of humic sites is not significantly modified by the complexation and  $\beta_{1,\text{IV}}$  can be expressed as:

$$\beta_{1,\text{IV}} \equiv \left( \frac{D^{\circ}}{D} - 1 \right) \frac{\alpha}{\text{LC} \times [\text{HA}(\text{IV})]_{\text{T}}} \quad (11).$$

The LC parameter cannot be determined straightforwardly from the available data because  $\text{Th}^{4+}$  saturation experiment was not, or rather could not, be undertaken in [50]. Hence, only the product  $\text{LC} \times \beta_{1,\text{IV}}$  could be calculated.

The pH, D and  $[\text{HA}]_{\text{T}}$  (eq/L) values from Nash and Choppin [50] are reported in Table 1.  $[\text{HA}(\text{IV})]_{\text{T}}$  is calculated as  $[\text{HA}]_{\text{T}}/4$ , according to the model. The values of the complexation coefficient  $\alpha$  are obtained from the thorium acetate complexation constants  $\beta_j^{\text{AcO}}$  available in [50, 62],  $\text{pK}_a(\text{AcO}^-) = 4.5$  and the thorium hydrolysis constants  $*\beta_i$  in [55] (Table 2).<sup>5</sup> A

<sup>5</sup> One should note that the strict application of SIT should require the knowledge of  $\text{Th}^{4+}/\text{CH}_3\text{COO}^-$  interaction parameter since the ionic medium is a mixture of  $\text{CH}_3\text{COONa}$  and  $\text{NaClO}_4$ .

mean value of  $\log(\text{LC} \times \beta_{1,IV}) = 11.7 \pm 0.3$  is obtained with a 95% confidence interval.<sup>6</sup> It is to be noted that the use of other constant sets [57, 59, 61] induces only minor changes, since the speciation of thorium (IV) is controlled by acetate complexation.

From the determination of LC in the case of neptunium (V), it has been observed that HAs from Gorleben (Gohy 573), Aldrich or Lac Bradford follow the same pattern [Fig. 8 in 65], yielding to the following expression:

$$\log \text{LC} = (0.26 \pm 0.03) \text{pH} - (2.72 \pm 0.02) \quad (12).$$

Otherwise, LC seems to increase with the charge of the metal (*e.g.*  $\text{Am}^{3+}$  - pH = 4, LC =  $0.216 \pm 0,007$  [28];  $\text{UO}_2^{2+}$  - pH = 4, LC =  $0.186 \pm 0,003$  [24];  $\text{NpO}_2^+$ , pH = 7, LC =  $0.13 \pm 0.01$  [65]). Unfortunately, the extrapolation to  $z = 4$  seems to be unreasonable because of the residual charges greater than  $z$  carried by the metals in actinyl (V) and (VI) molecular ions [66]. Furthermore, it is known that the loading parameter of  $\text{UO}_2\text{HA}(II)$  is close to the one of  $\text{Am}(\text{HA}(III))$  [24, 67-69]. The same behaviour was postulated in micellar exchange [70]. We propose to use LC = 0.2 in a first approximation as in the case of  $\text{Am}^{3+}$ . This leads to a value of  $\log \beta_{1,IV} = 12.4 \pm 0.3$  with a 95% confidence interval. Under these particular conditions, the value of LC does not seem to be as crucial as in the case of  $\text{Am}^{3+}$  [Fig. 7 in 28], as a value of LC = 0.3 would lead to a value of  $\log \beta_{1,IV} = 12.2$ , and  $\log \beta_{1,IV} = 12.7$  when LC = 0.1. The experimental uncertainty (2.6%) is without a doubt underestimated regarding to our approximations and possible systematic errors. Consequently, a 5% uncertainty should be a better estimate, leading to  $\log \beta_{1,IV} = 12.4 \pm 0.6$ .

The speciation of thorium (IV) using the specific interaction theory (SIT) [71], referring to the parameter in [61] (constants in Table 2) in 0.101 mol/kg water (*m*) (0.1 M  $\text{NaClO}_4$ ), could be proposed on Figure 1 when  $[\text{HA}(IV)]_T = 1.85 \cdot 10^{-5}$  eq/L,<sup>7</sup> close to the value for the Gorleben site Gohy 2227 [72]. The importance of humic complexation would then be limited to  $\text{pH} \leq 6.5$ , which is not in agreement with several environmental observations [36, 45-49].

In the framework of the CNM, the formation of a mixed hydrolysed complex could be postulated.

### 2.2.2. Mixed complex formation

Up to now only few studies considering mixed humic complexes of tetravalent actinides have been published. The first estimation was proposed in the case of plutonium (IV) in [73] considering the fact that more than 90% of tetravalent elements were complexed by HS in natural waters. The authors proposed the formation of  $\text{Pu}(\text{OH})_3\text{HA}(I)$  through:



<sup>6</sup>  $t_{0,95} = 2.201$ , with 12 values

<sup>7</sup> (HA) = 140 mg/L, PEC = 5.4 meq/g.

Up to now no validation of this estimate was done.

Recently, we studied the interaction of thorium (IV) with HS in a neutral pH range in competition with the silica surface [51]. These data could also be interpreted in the framework of the CNM. Adapting equations (8) and (9) leads to the following relations:

$$\beta_{1.3,l} = \frac{\alpha}{LC \times [\text{HA}(l)]_T \times [\text{OH}^-]^3} \left( \frac{D^\circ}{D} - 1 \right) = \frac{\alpha}{LC \times [\text{HA}(l)]_T \times 10^{3(\text{pH}-\text{pK}_w)}} \left( \frac{D^\circ}{D} - 1 \right) \quad (14).$$

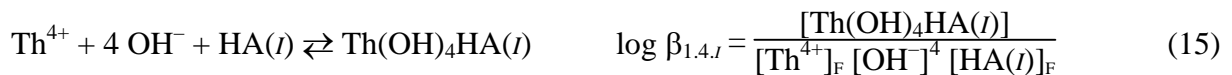
As in the case of  $\text{Am}^{3+}$ - $\text{Cm}^{3+}$  mixed complexes, we will consider that  $LC \equiv 1$  [52, 53]. The experimental results and estimated constants are reported in Table 3.

Contrary to  $\log \beta_{1,l}$ ,  $\log \beta_{1,n,l}$  directly depends upon the hydrolysis constant set since this phenomenon controls the aqueous speciation. Mean values of  $\log \beta_{1.3,l}$  of  $35.1 \pm 0.7$  [61] (Figure 2),  $36.7 \pm 0.8$  [55] to  $38.7 \pm 0.8$  [57] are obtained depending on the origin of the constants with 95% confidence interval. The  $\log \beta_{1.3,l}$  values are fairly constant in the pH range and seem to represent the pH influence on the humic complexation.

Speciation for  $[\text{HA}]_T = 7.8 \cdot 10^{-4}$  eq/L,<sup>8</sup> *i.e.* close to the Gorleben Gohy 2227 case, referring to [61] is proposed on Figure 3a under these assumptions. Compared with Figure 1, the predominance of humic complexes of thorium (IV) is clearly shifted by more than two pH units. When  $\text{pH} \geq 9$  the proportion of humic complex is still as high as 33%. If the HA concentration is reduced to  $[\text{HA}]_T = 6.00 \cdot 10^{-6}$  eq/L,<sup>9</sup> close to estimated value in Mont-Terri and Benken Swiss site [74] (Figure 3b), then humic complexes would represent 20% at  $\text{pH} = 7$  and around 3% at  $\text{pH} = 8$ .

Using a 95% confidence interval, the determinations  $\log \beta_{1.3,l}$  at different pH values are not significantly different. Nevertheless, a slight increase could be mentioned when accounting for  $\text{Th}(\text{OH})_3\text{HA}(l)$  (Figure 2). Two hypothesis could be made in the framework of the model: the occurrence of one less hydrolysed or one more hydrolysed species: *e.g.*  $\text{Th}(\text{OH})_2\text{HA}(l)$  and  $\text{Th}(\text{OH})_4\text{HA}(l)$  respectively. The former hypothesis is impossible to assess using these experimental data since  $\text{Th}(\text{OH})_2^{2+}$  would be predominant in solution when  $\text{pH} \leq 5.5$  [61]. The latter hypothesis needs an adaptation of the model. Through equation (2), if  $z = 0$  then  $[\text{HA}(l)] \rightarrow \infty$ . Hence, the boundary condition is when  $z = 0$  then  $[\text{HA}(l)] = [\text{HA}(l)]$ .

The following equilibrium could then be proposed:



The equation (14) is then rewritten as:

<sup>8</sup> (HA) = 140 mg/L, PEC = 5.4 meq/g,  $[\text{HA}(l)] = 7.4 \cdot 10^{-4}$  eq/L,  $[\text{HA}(IV)] \approx 1.9 \cdot 10^{-4}$  eq/L.

<sup>9</sup> (HA) = 0.6 mg/L, PEC = 5.4 meq/g,  $[\text{HA}(l)] = 3.23 \cdot 10^{-6}$  eq/L,  $[\text{HA}(IV)] \approx 1.08 \cdot 10^{-6}$  eq/L.

$$\beta_{1.4,l} = \frac{[\text{Th}(\text{OH})_4\text{HA}(l)]}{[\text{Th}^{4+}]_F [\text{OH}^-]^4 [\text{HA}(l)]_F} \equiv \frac{\alpha}{[\text{HA}(l)]_T \times 10^{4 \cdot (\text{pH} - \text{pK}_w)}} \left( \frac{K_d^o}{K_d} - 1 \right) \quad (16)$$

The calculated values of  $\log \beta_{1.4,l}$  are also reported in Table 3. Like in the case of  $\log \beta_{1.3,l}$ ,  $\log \beta_{1.4,l}$  directly depends on the hydrolysis constant set. Mean values of  $\log \beta_{1.4,l}$  of  $41.6 \pm 0.6$  [61],  $43.2 \pm 0.6$  [55] and  $45.2 \pm 0.6$  [57] are obtained depending on the origin of the constants. Nevertheless, a slight decrease in  $\log \beta_{1.4,l}$  with pH could be noted (Figure 2). The data could then be described with more than one species – *e.g.*  $\text{Th}(\text{OH})_3\text{HA}(l)$  and  $\text{Th}(\text{OH})_4\text{HA}(l)$  –, but the constants could not be assessed with the experimental data.

A speciation is calculated with  $[\text{HA}]_T = 7.8 \cdot 10^{-4}$  eq/L on Figure 4a, with  $\log \beta_{1.4,l} = 41.6$ . HA totally controls the thorium chemistry when  $\text{pH} \leq 10$ . The proportion of humic complex is still important when (HA) is lowered to 0.3 mg/L or  $[\text{HA}]_T = 1.48 \cdot 10^{-6}$  eq/L (Swiss site, Figure 4b). This result does not seem to be in agreement with the results of the study of Glaus *et al.* [74], but one must remind that the carbonate complexation has not been taken into account.

The original sorption results in [51] could help us to opt for an hypothesis. Both  $D^o$  and  $D$  values of thorium (IV) in the systems Th-SiO<sub>2</sub>-HA are very similar at the three pH values (*i.e.* 6.75, 7.2, 7.9). This fact may indicate that the complexation properties of HA towards thorium (IV) are rather constant in the pH range. This may be in favour of the  $\text{Th}(\text{OH})_4\text{HA}(l)$  option, which implies a rather constant proportion of humic complex when  $\text{pH} \geq 6.7$ .

### 2.3. Application to solubility prediction and on independent data

One could calculate the enhancement of the “theoretical” solubility of  $\text{ThO}_2(\text{cr})$  referring to the values in [61] in the case of Gohy 2227 (Figure 5). A fairly high enhancement of thorium solubility could be prognosticated. In the case of the Swiss sites the enhancement is lower than the uncertainty of the  $\text{ThO}_2$  solubility (data not shown). Like it has already been observed in the case of Fe, [75, 76], Al [77] and Pd [78], an increase of more than one order of magnitude could be expected. The same trend could be observed for the other actinide oxides. An experimental validation of this hypothesis is needed.

The formation of carbonate complexes of thorium is a matter of debate. Some authors proposed the limiting carbonate complex  $\text{Th}(\text{CO}_3)_5^{6-}$  [56, 58, 79], as it is the case for uranium (IV) [71], plutonium (IV) [80] and neptunium (IV) [81]. From solubility experiments of  $\text{ThO}_2$  in carbonate media, the formation of  $\text{ThCO}_3(\text{OH})_3^-$  was also proposed [58, 82] at low carbonate concentration, even if spectroscopic evidences of this species could not be obtained [82].

Even if the formation of mixed complexes is also a matter of debate [83-85], we can use these constants in order to appreciate the effects of carbonate complexation of thorium (IV) on the stability of humic complexes. We calculated a speciation for a total inorganic carbon concentration,  $[\text{TIC}] = 8.2 \cdot 10^{-3}$  m,  $[\text{HA}]_T = 7.4 \cdot 10^{-4}$  eq/L, using the  $\text{Th}^{4+}$  hydrolysis and carbonation constants in [57, 58] extrapolated to 0.101 m (0.1 M NaClO<sub>4</sub>) using the SIT parameters in [71], the associated humic constants  $\log \beta_{1,lV} = 12.4$ ,  $\log \beta_{1.3,l} = 38.7$  (Figure 6a)

or  $\log \beta_{1.4,l} = 45.2$  (Figure 6b). When  $\text{Th}(\text{OH})_3\text{HA}(l)$  is taken into account, the mixed carbonato complex limits the domain where the humic complexation controls thorium chemistry. Nevertheless, the humic complex represents 60% of total thorium (IV) at  $\text{pH} = 8$  (Figure 6a). Conversely, when  $\text{Th}(\text{OH})_4\text{HA}(l)$  is considered,  $\text{ThCO}_3(\text{OH})_3^-$  only decrease the proportion of  $\text{Th}(\text{OH})_4\text{HA}(l)$  to 90% ( $\approx 100\%$  without carbonate, Figure 6b). This latter result seems to be more relevant of natural situations where thorium is associated to natural organic matter in the presence of carbonate ions [42, 51, 72]. The formation of mixed hydroxycarbonato complexes is not likely because of the negative charge of these complexes that are repelled by the negative charge of the humic acid entities. Particularly, this is the case for carbonato complexes of uranium (VI) [54], and for the influence of iodide onto the electrophilic substitution of iodine on phenolic moieties of HA [86, 87].

An application to the works of Glaus *et al.* [74] leads now to the same weak interaction of thorium (IV) with Mont-Terri and Benken organic matters as already calculated in [51] ( $\text{Th}(\text{OH})_4\text{HA}(l) \leq 3\%$ ), Figure 6c).<sup>10</sup>

These reinterpretations of the literature data provide a consistent view of the environmental behaviour of thorium (IV). Nevertheless, further works are needed in order to assess these points experimentally.

In the following we will use the complexes  $\text{MHA}(IV)$  with  $\log \beta_{1,IV} = 12.4$  and  $\text{M}(\text{OH})_4\text{HA}(l)$  with  $\log \beta_{1.4,l}$  adapted to the hydrolysis constants sets.

### 3. Application to redox sensitive actinide elements

The use of analogy between elements is useful when it is a matter of estimating data on difficult systems like uranium, neptunium or plutonium [1, 88, 89]. In deep geological media, these elements are supposed to be stable in their reduced form *i.e.* neptunium (IV), uranium (IV) and plutonium (IV) - plutonium (III) [81, 90]. If data on americium (III) or curium (III) and uranium (VI) exist in the literature [24, 67], there is only one communication up to now on neptunium (IV) complexation by HA in neutral pH interpreted with CNM [44]. The authors report an “increasing” constant in the case of  $\text{Np}(\text{OH})_3\text{HA}(l)$  and  $\log \beta_{1.4,l} = 52$  independent of pH ( $6 \leq \text{pH} \leq 9.5$ ). The neptunium (IV) hydrolysis data are not referred in the abstract.

If one assumes that the results obtained with thorium (IV) [51] can mimic those that may be acquired in the case of uranium (IV), neptunium (IV) or plutonium (IV), then using equation (11) and (16), with the proper  $\alpha$  values and the hydrolysis constant extrapolated to 0.101 *m*  $\text{NaClO}_4$  [71, 81], would give a reasonable estimates of  $\beta_{1,IV}$  and  $\beta_{1.4,l}$ . we can propose the value of  $\log \beta_{1.4,l} = 49.3$  in the case of neptunium (IV). This value is somewhat lower than the results of [44]. In as much, we can propose  $\log \beta_{1.4,z}$  values of 54.4 referring to [71] and

<sup>10</sup> 12.5 mg/L  $\leq$  (NOM)  $\leq$  5.5 mg/L, comprising around 5% HA

52.1 referring to [81 page 323]<sup>11</sup> in the case of uranium (IV) and plutonium (IV) respectively. One could note that these proposed constants agree with the order of affinity proposed in [91]. Furthermore, thorium (IV) and plutonium are known to have the same behaviour in presence of natural organic matter [92]. Nevertheless, readers should bear in mind that these constants are only estimates and should be used with caution.

An exercise on the chemistry of uranium, neptunium and plutonium in waters that contains high HA concentration could be proposed. The complexation constants from  $\text{Am}^{3+}/\text{Cm}^{3+}/\text{Eu}^{3+}$  are very similar to one another [43, 67]. Then using  $\log \beta_{1,III} = 6.2$  seems to be a fair approximation in the case of  $\text{Pu}^{3+}$  or  $\text{Np}^{3+}$ . The constants of the mixed complexes evidenced in [52, 53] can also be used without modification for  $\text{Pu}^{3+}$ , *i.e.*  $\log \beta_{1,1,II} \approx 13$  and  $\log \beta_{1,2,I} \approx 17.6$ . In the case of the carbonato complex, the estimation of  $\text{Pu}(\text{CO}_3)_m^{3-2m}$  in [93], very close to the values recommended for  $\text{Am}^{3+}$  [94], and the mixed complex postulated in [52], will be applied without any modification. The upper limit constant for the formation of mixed carbonato complex  $\text{Pu}(\text{CO}_3)_2(\text{OH})_3^{3-12}$ ,<sup>12</sup> used by Vitorge and Capdevila [88] to fit the  $\text{PuO}_2(\text{s})$  solubility in carbonate media from literature was also included.

For actinyl (V) and (VI) ions, the values for neptunium (V) obtained at low concentration [25, 38, 39], and uranium (VI) [24, 54], could be directly applied to plutonium (V) and adapted to plutonium (VI). The constants calculated from the original data at 0.101 *m*  $\text{NaClO}_4$  referring to plutonium (VI), neptunium (V) and uranium (VI) are also reported in Table 4. These constants were used in the analytical resolutions of the systems.

It is also reminded to the reader that the reducing capacity of HS is not taken into account in these calculations, as this behaviour is still difficult to assess [3-5] and is dependent on light exposure [9, 95].

Speciation of plutonium (Figure 7), neptunium (Figure 8) and uranium (Figure 9) was calculated for  $E_H = -30$  mV/SHE,  $[\text{TIC}] = 8.2 \cdot 10^{-3}$  *m*,  $6 \leq \text{pH} \leq 10$ ,  $[\text{HA}]_T = 0$  and  $5.4 \cdot 10^{-4}$  eq/L,<sup>13</sup> assuming that  $\text{LC} = \text{LC}(\text{Am}^{3+})$  for all humic complexes [Fig. 3 in 67] except for  $\text{MO}_2\text{HA}(I)$  [Eq. 14 in 65]. As expected, under these particular conditions, mixes of redox species could be observed. For each actinide, a shift in the predominance of M(III) and M(IV) towards higher pH values in the presence of HA could be observed, due to the formation of the mixed complexes. The formation of  $\text{NpHA}(III)$  or  $\text{NpOHHA}(II)$  only occurs below the reduction limit of water and these complexes are not reported.

The theoretical speciation *vs.*  $E_H$  (mV/SHE) at  $\text{pH} = 7$ ,  $[\text{TIC}] = 8.2 \cdot 10^{-3}$  *m* and  $[\text{HA}]_T = 5.4 \cdot 10^{-4}$  eq/L ( $\text{HA} = 100$  mg/L) for neptunium, plutonium and uranium (Figure 10) can also be calculated. It can be seen that neptunium could coexist as  $\text{NpO}_2\text{HA}(I)$  and  $\text{Np}(\text{OH})_4\text{HA}(I)$ , and that it could be totally reduced to  $\text{Np}(\text{OH})_4\text{HA}(I)$  when  $E_H \leq 0$  mV/SHE (Figure 10a). This can be related with the observation from Gorleben ground waters [54]. Furthermore, the

<sup>11</sup>  $\log \beta^\circ(\text{Pu}(\text{OH})_4(\text{aq})) = -6.9$

<sup>12</sup>  $\text{Pu}^{4+} + 2\text{CO}_3^{2-} + 3\text{OH}^- \rightleftharpoons \text{Pu}(\text{CO}_3)_2(\text{OH})_3^{2-}$ ,  $\log \beta < 50.5$

<sup>13</sup>  $(\text{HA}) \approx 100$  mg/L

formation of NpHA(IV) would impede the reduction to neptunium (III) when  $\text{pH} \leq 5$  (data not shown).

In the case of Pu (Figure 10b), plutonium (III) humic complexation could be significant when  $E_H \leq 100$  mV/SHE and may lead to mixes of plutonium oxidation states in solution, as it has already been reported [96, 97]. The other redox behaviour of plutonium reported in [10, 11] are more difficult to assess with these data. Nevertheless, different authors have measured  $E_H$  for different humic acid solutions at  $\text{pH} = 7$ :  $E_H \approx + 230$  mV/SHE [4];  $E_H \approx + 260$  mV/SHE [98];  $300 \leq E_H$  (mV/SHE)  $\leq 400$  [99];  $438 \leq E_H$  (mV/SHE)  $\leq 407$  [100]. Under these conditions, plutonium is stable as Pu(OH)<sub>4</sub>HA(*l*), and plutonium (VI) or plutonium (V) introduced could be reduced and then complexed by HA.

In the case of uranium (Figure 10c), the formation of U(OH)<sub>4</sub>HA(*l*) could also imply a shift in the predominance of uranium (IV) towards higher pH values. The negative carbonate complexes of uranium (VI) would impede the formation of the humic complex [54, 69]. The reduction of uranium (VI) would only be possible when  $E_H \leq 80$  mV/SHE. This value is higher than the measured ones [4, 98-100] and gives a plausible explanation for the absence of reaction noted by several authors [24, 25]. One should note that the behaviour of UO<sub>2</sub>OHHA(*l*) and PuO<sub>2</sub>OHHA(*l*) are not the same due to the highest value for the constant for PuO<sub>2</sub>CO<sub>3</sub>(aq) compared to UO<sub>2</sub>CO<sub>3</sub>(aq) [81, 94], probably due to systematic uncertainty [Vitorge, Pers. Comm.]. This cannot be considered as representative of plutonium (VI) compartment in sea water [12]. Furthermore, one can notice that there is a marked difference between the experimental data from different authors for uranium (VI) under low CO<sub>2</sub>(g) partial pressure.<sup>14</sup> Zeh *et al.* [54] did not evidenced relevant humic interaction when  $\text{pH} \geq 9$ , while Glaus *et al.* [68, 69] and Laszak [101] quantified a significant interaction up to  $\text{pH} = 10$ . The humic interaction of M(VI) cations could therefore be underestimated in neutral to alkaline media. Further works are needed to ascertain this point.

Nevertheless, in the case of uranium, neither the results of Li *et al.* [102], nor those from Artinger *et al.* [26] could be assessed by this exercise. In the latter study, the authors did not observe any difference in the behaviour of uranium, introduced as uranium (VI) or uranium (IV), neither with purified HA [102], nor with Gorleben groundwater in the presence of natural organic matter at varying  $E_H$  [26].<sup>15</sup> Under these conditions, the uranium speciation would predict U(OH)<sub>4</sub>HA(*l*) as predominant species up to  $E_H = -20$  mV/SHE, and carbonate uranium (VI) complexes for higher potentials (data not shown). More results on the actual interaction of uranium (IV) with natural organic matter under well-controlled redox conditions are thus required in order to assess this point.

$E_H$ -pH diagrams could also be proposed in a closed system consisting of  $10^{-10}$  mole actinide/kg water,  $8.2 \cdot 10^{-3}$  mole total carbonate/kg water and 100 mg HA/L (PEC = 5.4 meq/L). Here again we must recall that these diagrams are only the results of speciation

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<sup>14</sup>  $\log(\text{pCO}_2) = -6$

<sup>15</sup>  $-200 \leq E_H$  (mV/SHE)  $\leq +150$ ,  $\text{pCO}_2 = 1\%$ ,  $\text{pH} = 7.2$ .

calculations and does not take into account the redox properties of HS, and cannot be considered as strict representation of actinide compartment in the presence of HS. The most striking example is the lack of plutonium (VI) humic complexation when  $\text{pH} \geq 4.5$  as it has been observed in sea water [12].

Finally, the ability of actinides (IV) to form colloids – so called “real-colloids” –, or to be associated with mineral and/or organic colloids – pseudo-colloids – in solution is not taken into account in this exercise [103]. The adsorption of actinides in general, and actinides (IV) in particular, on these colloidal phases is a known problem [10, 104-106]. So does is the stabilisation of mineral colloids by the sorption of organic matter [107-109]. An interesting study on this account is the one reported in Santschi *et al.* [92]. The authors clearly showed that Pu – most certainly Pu(IV) as it behave like Th(IV) – in pond release waters and stormwater runoff in Rocky Flats Environmental Technology Site is significantly associated<sup>16</sup> to the organic part of the colloids,  $< 0.5 \mu\text{m}$  in size. These organic colloids contained neither Si nor Al and only a weak amount of Fe, enhancing the fact that the natural chemistry of actinides (IV) is greatly influenced by natural organic matter. Nonetheless, the formation of humic coated surface, or so called organoclays, is still difficult to describe by available modelling approaches [110].

#### 4. Conclusions

Through this exercise, we outlined that the use of analogy could permit to estimate the missing humic acid complexation constants for redox sensitive elements, namely uranium, neptunium and plutonium. Reinterpretations of thorium (IV) data available in the literature allowed us to have consistent data sets for this element and to represent independent environmental data. The adaptation of these data through analogy for uranium (IV), neptunium (IV) and plutonium (IV), permitted us to propose humic interaction constant that could be used for prognosticating the chemical form of redox sensitive actinides in environmental systems. The transposition of available data on uranium (VI), neptunium (V) and americium-curium-europium (III) helped us to appreciate the humic complexation of the different redox states of plutonium, neptunium and uranium. We have shown that the use of these data and analogies could permit to understand some puzzling behaviour of these elements.

Nevertheless, some results still cannot be represented as in the case of marine systems for plutonium and deep groundwater systems for uranium, enhancing the fact that more experiments are needed to ascertain the influence of natural organic matter onto the redox chemistry of this element.

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<sup>16</sup> 7 to 66% of the total Pu pool.

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## 6. References

1. Choppin, G. R.: Utility of oxidation state analogs in the study of plutonium behavior. *Radiochim. Acta* **85**, 89 (1999).
2. David, F.: Thermodynamic properties of lanthanide and actinide ions in aqueous solution. *J. Less Common Metals* **121**, 27 (1986).
3. Wahlberg, O., Ågren, S.: Studies of fulvic and humic acids .1. Determination of the steady states for slow processes in 0.1 M NaCl aqueous solution at 25 degrees C. *Acta Chem. Scand.* **50**, 561 (1996).
4. Österberg, R., Shirshova, L.: Oscillating, nonequilibrium redox properties of humic acids. *Geochim. Cosmochim. Acta* **61**, 4599 (1997).
5. Aguer, J.-P., Richard, C., Andreux, F.: Comparison of the photoinductive properties of commercial, synthetic and soil-extracted humic substances. *J. Photochem. Photobiol. A* **103**, 163 (1997).
6. Kim, J. I., Delakowitz, B., Zeh, P. D., Koltz, D., Lazik, D.: A column experiment for the study of colloidal radionuclide migration in Gorleben aquifer systems. *Radiochim. Acta* **66/67**, 165 (1994).
7. Zeh, P., Kim, J. I., Marquardt, C. M., Artinger, R.: The reduction of Np(V) in groundwater rich in humic substances. *Radiochim. Acta* **87**, 23 (1999).
8. Artinger, R., Marquardt, C. M., Kim, J. I., Seibert, A., Trautman, N., Kratz, J. V.: Humic colloid-borne Np migration: influence of the oxidation state. *Radiochim. Acta* **88**, 609 (2000).
9. André, C., Choppin, G. R.: Reduction of Pu(V) by humic acid. *Radiochim. Acta* **88**, 613 (2000).
10. Sanchez, A. L., Murray, J. M., Sibley, T. H.: The adsorption of plutonium IV and V on goethite. *Geochim. Cosmochim. Acta* **49**, 2297 (1985).
11. Nash, K. L., Fried, S., Friedman, A. M., Sullivan, J. C.: Redox behavior, complexing, and adsorption of hexavalent actinides by humic acid and selected clays. Stiring marine disposal of high-level radioactive waste. *Environ. Sci. Technol.* **15**, 834 (1981).
12. Garcia, K., Boust, D., Moulin, V., Douville, E., Fourest, B., Guillaumont, R.: Multiparametric investigation of the reactions of plutonium under estuarine conditions. *Radiochim. Acta* **74**, 165 (1996).
13. Miles, C. J., Brezonik, P. L.: Oxygen consumption in humic-colored waters by a photochemical ferrous-ferric catalytic cycle. *Environ. Sci. Technol.* **15**, 1089 (1981).
14. Skogerboe, R. K., Wilson, S. A.: Reduction of ionic species by fulvic acid. *Anal. Chem.* **53**, 228 (1981).
15. Liang, L., McNabb, J. A., Paulk, J. M., Gu, B., McCarthy, J. F.: Kinetics of Fe(II) oxygenation at low partial pressure of oxygen in the presence of natural organic matter. *Environ. Sci. Technol.* **27**, 1864 (1993).
16. Liang, L., McCarthy, J. F., Jolley, L. W., McNabb, J. A., Mehlhorn, T. L.: Iron dynamics: transformation of Fe(II)/Fe(III) during injection of natural organic matter in a sandy aquifer. *Geochim. Cosmochim. Acta* **57**, 1987 (1993).
17. Spokes, L. J., Liss, P. S.: Photochemically induced redox reactions in seawater .1. Cations. *Mar. Chem.* **49**, 201 (1995).
18. Lu, X., Johnson, W. D., Hook, J.: Reaction of vanadate with aquatic humic substances: an ESR and <sup>51</sup>V NMR Study. *Environ. Sci. Technol.* **32**, 2257 (1998).
19. Nakayasu, K., Fukushima, M., Sasaki, K., Tanaka, S., Nakamura, H.: Comparative studies of the reduction behavior of chromium(VI) by humic substances and their precursors. *Environ. Toxicol. Chem.* **18**, 1085 (1999).
20. Al Mahamid, I., Becraft, K. A., Nitsche, H.: Complexation of plutonium(V) with nitrilotriacetic acid. *Radiochim. Acta* **68**, 63 (1995).
21. Al Mahamid, I., Becraft, K. A., Hakem, N. L., Gatti, R. C., Nitsche, H.: Stability of various plutonium valence states in the presence of NTA and EDTA. *Radiochim. Acta* **74**, 129 (1996).

22. Bion, L., Moisy, P., Vaufrey, F., Meot-Reymond, S., Simoni, E., Madic, C.: Coordination of  $U^{4+}$  in the complex  $U(P_2W_{17}O_{61})_2^{16-}$  in solid state and in aqueous solution. *Radiochim. Acta* **78**, 73 (1997).
23. Reed, D. T., Wygmans, D. G., Aase, S. B., Banaszak, J. E.: Reduction of Np(VI) and Pu(VI) by organic chelating agents. *Radiochim. Acta* **82**, 109 (1998).
24. Czerwinski, K. R., Buckau, G., Scherbaum, F., Kim, J. I.: Complexation of the uranyl ion with aquatic humic acid. *Radiochim. Acta* **65**, 111 (1994).
25. Moulin, V., Tits, J., Laszak, I., Moulin, C., Decambox, P., de Ruty, O.: Complexation behaviour of humic substances studied by Time-Resolved Laser-Induced Fluorescence and Spectrophotometry. Commission of the European Communities, Report EUR 16843 EN, Brussels (1996).
26. Artinger, R., Rabung, T., Kim, J. I., Sachs, S., Schmeide, K., Heise, K. H., Bernhard, G., Nitsche, H.: Humic colloid-borne migration of uranium in sand columns. *J. Contam. Hydrol.* **58**, 1 (2002).
27. Choppin, G. R., Kullberg, L.: Protonation thermodynamics of humic acid. *J. Inorg. Chem.* **40**, 651 (1978).
28. Kim, J. I., Czerwinski, K. R.: Complexation of metal ions with humic acid: metal ion charge neutralization model. *Radiochim. Acta* **73**, 5 (1996).
29. Tipping, E.: Humic ion-binding model VI: An improved description of the interactions of protons and metal ions with humic substances. *Aquat. Geochem.* **4**, 3 (1998).
30. Kinniburgh, D. G., van Riemsdijk, W. H., Koopal, L. K., Borkovec, M., Benedetti, M. F., Avena, M. J.: Ion binding to natural organic matter: competition, heterogeneity, stoichiometry and thermodynamic consistency. *Colloid Surf. A-Physicochem. Eng. Asp.* **151**, 147 (1999).
31. Kinniburgh, D. G., Milne, C. J., Benedetti, M. F., Pinheiro, J. P., Filius, J., Koopal, L. K., van Riemsdijk, W. H.: Metal ion binding by humic acid: application of the NICA-Donnan model. *Environ. Sci. Technol.* **30**, 1687 (1996).
32. Pinheiro, J. P., Mota, A. M., Benedetti, M. F.: Lead and calcium binding to fulvic acids: salt effect and competition. *Environ. Sci. Technol.* **33**, 3398 (1999).
33. Plancque, G., Amekraz, B., Moulin, V., Toulhoat, P., Moulin, C.: Molecular structure of fulvic acids by electrospray with quadrupole time-of-flight mass spectrometry. *Rapid Commun. Mass Spectrom.* **15**, 827 (2001).
34. Piccolo, A., Nardi, S., Concheri, G.: Micelle-like conformation of humic substances as revealed by size exclusion chromatography. *Chemosphere* **33**, 595 (1996).
35. Tipping, E.: Modelling the competition between alkaline earth cations and trace metal species for binding by humic substances. *Environ. Sci. Technol.* **27**, 520 (1993).
36. Zeh, P., Kim, J. I., Buckau, G. Aquatic colloids composed of humic substances, Binding models concerning natural organics in performance assessment. OECD NEA Proceedings, (1995).
37. Kim, J. I., Sekine, T.: Complexation of neptunium(V) with humic acid. *Radiochim. Acta* **55**, 187 (1991).
38. Marquardt, C., Herrman, G., Trautmann, N.: Complexation of neptunium(V) with humic acids at very low concentrations. *Radiochim. Acta* **73**, 119 (1996).
39. Seibert, A., Mansel, A., Marquardt, C. M., Keller, H., Kratz, J. V., Trautmann, N.: Complexation behaviour of neptunium with humic acid. *Radiochim. Acta* **89**, 505 (2001).
40. Buckau, G., Kim, J. I., Klenze, R., Rhee, D. S., Wimmer, H.: A comparative spectroscopic study of the fulvate complexation of trivalent transuranium ions. *Radiochim. Acta* **57**, 105 (1992).
41. Kim, J. I., Rhee, D. S., Wimmer, H., Buckau, G., Klenze, R.: Complexation of trivalent actinide ions ( $Am^{3+}$ ,  $Cm^{3+}$ ) with humic acid: a comparison of different experiment methods. *Radiochim. Acta* **62**, 35 (1993).
42. Kim, J. I., Rhee, D. S., Buckau, G., Morgenstern, A.: Americium(III)-humate interaction in natural groundwater: Influence of purification on complexation properties. *Radiochim. Acta* **79**, 173 (1997).
43. Shin, H. S., Lee, B. H., Choi, J. G., Moon, H.: Complexation of soil humic-acid with trivalent curium and europium ions: a comparative study. *Radiochim. Acta* **69**, 185 (1995).
44. Pirlet, V., Delécaut, G. Complexation of Np(IV) with humic acids at hydrolysis pH range: determination of complexation constants. 9<sup>th</sup> International Conference on Chemistry and Migration Behavior of Actinides and Fission Products in the Geosphere, Migration '03. September 21-26, 2003, Gyeongju, Korea (2003).
45. Miekeley, N., Vale, M. G. R., Tavares, T. M., Lei, W.: Some aspects of the influence of surface and ground water chemistry on the mobility of thorium in the "Morro do Ferro" - environment. *Mat. Res. Soc. Symp. Proc.* **11**, 725 (1982).

46. Miekeley, N., Dotto, R. M., Kuchler, I. L., Insalta, P.: The importance of organic compounds on the mobilization and bioassimilation of thorium in the Morro do Ferro environment. *Mat. Res. Soc. Symp. Proc.* **44**, 591 (1985).
47. Niven, S. E. H., Moore, R. M.: Effect of natural colloidal matter on the equilibrium adsorption of thorium in seawater. In: *Radionuclides: A tool for Oceanography* (Guary, J. C. ed.) Elsevier, (1988) p. 111.
48. Nordén, M., Albinsson, Y., Ephraim, J. H., Allard, B.: A comparative study of europium, thorium and uranium binding to an aquatic fulvic acid. *Material Research Society Symposia Proceeding* **294**, 759 (1993).
49. Dai, M. H., Benitez-Nelson, C. R.: Colloidal organic carbon and  $^{234}\text{Th}$  in the Gulf of Maine. *Mar. Chem.* **74**, 181 (2001).
50. Nash, K. L., Choppin, G. R.: Interaction of humic and fulvic acids with Th(IV). *J. Inorg. Nucl. Chem.* **42**, 1045 (1980).
51. Reiller, P., Moulin, V., Casanova, F., Dautel, C.: On the study of Th(IV)-humic acid interactions by competition sorption studies with silica and determination of global interaction constants. *Radiochim. Acta* **91**, 513 (2003).
52. Panak, P., Klenze, R., Kim, J. I.: A study of ternary complexes of Cm(III) with humic acid and hydroxyde or carbonate in neutral pH range by time resolved laser fluorescence spectroscopy. *Radiochim. Acta* **74**, 141 (1996).
53. Morgenstern, M., Klenze, R., Kim, J. I.: The formation of mixed-hydroxo complexes of Cm(III) and Am(III) with humic acid in the neutral pH range. *Radiochim. Acta* **88**, 7 (2000).
54. Zeh, P., Czerwinski, K. R., Kim, J. I.: Speciation of uranium in Gorleben groundwaters. *Radiochim. Acta* **76**, 37 (1997).
55. Baes, C. F., Mesmer, R. E.: *The hydrolysis of cations*. Wiley Interscience Publication, New-York (1976).
56. João, A., Bigot, S., Fromage, F.: Étude des carbonates complexes des éléments IVB I - Détermination de la constante de stabilité du pentacarbonatothorate (IV). *Bull. Soc. Chim. France* **42** (1987).
57. Grenthe, I., Lagerman, B.: Studies on metal carbonate equilibria. 23. Complex formation in the Th(IV)-H<sub>2</sub>O-CO<sub>2</sub>(g) system. *Acta Chim. Scand.* **45**, 231 (1991).
58. Östholms, E., Bruno, J., Grenthe, I.: On the influence on mineral dissolution: III. The solubility of microcrystalline ThO<sub>2</sub> in CO<sub>2</sub>-H<sub>2</sub>O media. *Geochim. Cosmochim. Acta* **58**, 613 (1994).
59. Ekberg, C., Albinsson, Y., Comarmond, M. J., Brown, P. L.: Studies on the complexation behavior of thorium(IV). 1. Hydrolysis equilibria. *J. Solut. Chem.* **29**, 63 (2000).
60. Moulin, C., Amekraz, B., Hubert, S., Moulin, V.: Study of thorium hydrolysis species by electrospray-ionization mass spectrometry. *Anal. Chim. Acta* **441**, 269 (2001).
61. Neck, V., Kim, J. I.: Solubility and hydrolysis of tetravalent actinides. *Radiochim. Acta* **89**, 1 (2001).
62. Portanova, R., diBernardo, P., Traverso, O., Mazzochin, A., Magon, L.: Thermodynamic properties of actinide complexes. 2. Thorium(IV)-acetate system. *J. Inorg. Nucl. Chem.* **37**, 2177 (1975).
63. Schubert, J.: *J. Phys. Coll. Chem.* **52**, 340 (1948).
64. Schubert, J., Richter, J. W.: *J. Phys. Coll. Chem.* **52**, 350 (1948).
65. Marquardt, C., Kim, J. I.: Complexation of Np(V) with humic acid: Intercomparison of results from different laboratories. *Radiochim. Acta* **80**, 129 (1998).
66. Choppin, G. R., Rao, L. F.: Complexation of pentavalent and hexavalent actinides by fluoride. *Radiochim. Acta* **37**, 143 (1984).
67. Czerwinski, K. R., Kim, J. I., Rhee, D. S., Buckau, G.: Complexation of trivalent actinides ions (Am<sup>3+</sup>, Cm<sup>3+</sup>) with humic acids: the effect of ionic strength. *Radiochim. Acta* **72**, 179 (1996).
68. Glaus, M. A., Hummel, W., Van Loon, L. R.: Trace metal-humate interactions. I. Experimental determination of conditional stability constants. *Appl. Geochem.* **15**, 953 (2000).
69. Hummel, W., Glaus, M. A., Van Loon, L. R.: Trace metal-humate interaction. II. The conservative roof model and its application. *Appl. Geochem.* **15**, 975 (2000).
70. Reiller, P., Moulin, C., Beaucaire, C., Lemordant, D.: Dual use of micellar enhanced ultrafiltration and time-resolved laser-induced spectrofluorometry for the study of uranyl exchange at the surface of alkylsulfate micelles. *J. Colloid Interface Sci.* **163**, 81 (1994).
71. Grenthe, I., Fuger, L., Konings, R. G. M., Lemire, R. J., Muller, A. B., Nguyen-Trung, C., Wanner, H.: *Chemical thermodynamics of uranium*. North-Holland, Amsterdam (1992).

72. Kim, J. I., Marquardt, C. M.: Chemical reaction of Np(V) with humic colloids in groundwater: Influence of purification on the complexation behaviour. *Radiochim. Acta* **87**, 105 (1999).
73. Czerwinski, K., Kim, J. I.: Complexation of transuranic ions by humic substances: application of laboratory results to the natural system. *Mat. Res. Soc. Symp. Proc.* **465**, 743 (1997).
74. Glaus, M. A., Baeyens, B., Lauber, M., Rabung, T., van Loon, L. R.: Water-extractable organic matter from opalinus clay: effect on sorption and speciation of Ni(II), Eu(III) and Th(IV). Paul Scherrer Institut, Report 01-14, Villigen (2001).
75. Rose, J., Vilge, A., Olivie-Lauquet, G., Masion, A., Fréchet, C., Bottero, J. Y.: Iron speciation in natural organic matter colloids. *Colloid Surf. A-Physicochem. Eng. Asp.* **136**, 11 (1998).
76. Vilgé-Ritter, A., Rose, J., Masion, A., Bottero, J. Y., Laine, J. M.: Chemistry and structure of aggregates formed with Fe-salts and natural organic matter. *Colloid Surf. A-Physicochem. Eng. Asp.* **147**, 297 (1999).
77. Masion, A., Vilge-Ritter, A., Rose, J., Stone, W. E. E., Teppen, B. J., Rybacki, D., Bottero, J. Y.: Coagulation-flocculation of natural organic matter with Al salts: Speciation and structure of the aggregates. *Environ. Sci. Technol.* **34**, 3242 (2000).
78. Wood, S. A., Tait, D. C., Vlassopoulos, D., Janecky, D. R.: Solubility and spectroscopic studies of the interaction of palladium with simple carboxylic acids and fulvic acid at low temperature. *Geochim. Cosmochim. Acta* **58**, 625 (1994).
79. Rai, D., Felmy, A. R., Moore, D. A., Mason, M. J.: The solubility of Th(IV) and U(IV) hydrous oxides in concentrated NaHCO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> solutions. *Mat. Res. Soc. Symp. Proc.* **353**, 1143 (1995).
80. Capdevila, H., Vitorge, P., Giffaut, E., Delmau, L.: Spectrophotometric study of the dissociation of the Pu(IV) carbonate limiting complex. *Radiochim. Acta* **74**, 93 (1996).
81. Lemire, R. J., Fuger, J., Nitsche, H., Potter, P., Rand, M., Rydberg, J., Spahiu, K., Sullivan, J. C., Ullman, W. J., Vitorge, P., Wanner, H.: *Chemical thermodynamics of neptunium and plutonium*. North Holland, Amsterdam (2001).
82. Felmy, A. R., Rai, D., Sterner, S. M., Mason, M. J., Hess, N. J., Conradson, S. D.: Thermodynamic models for highly charged aqueous species: Solubility of Th(IV) hydrous oxide in concentrated NaHCO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> solutions. *J. Solut. Chem.* **26**, 233 (1997).
83. Bruno, J., Stumm, W., Wersin, P., Brandberg, F.: On the influence of carbonate in mineral dissolution: I. The thermodynamics and kinetics of hematite dissolution in bicarbonate solution at T = 25 °C. *Geochim. Cosmochim. Acta* **56**, 1139 (1992).
84. Hummel, W.: Comment on "On the influence of carbonate in mineral dissolution: 1. The thermodynamics and kinetics of hematite dissolution in bicarbonate solutions at T=25 degrees C" by J. Bruno, W. Stumm, P. Wersin, and F. Brandberg. *Geochim. Cosmochim. Acta* **64**, 2167 (2000).
85. Bruno, J., Duro, L.: Reply to W. Hummel's comment on and correction to "On the influence of carbonate in mineral dissolution: 1. The thermodynamics and kinetics of hematite dissolution in bicarbonate solutions at T=25 degrees C" by J. Bruno, W. Stumm, P. Wersin, and F. Brandberg. *Geochim. Cosmochim. Acta* **64**, 2173 (2000).
86. Warner, J. A., Casey, W. H., Dahlgren, R. A.: Interaction kinetics of I<sub>2</sub>(aq) with substituted phenols and humic substances. *Environ. Sci. Technol.* **34**, 3180 (2000).
87. Reiller, P., Moulin, V.: Influence of organic matter in the prediction of iodine migration in natural environment. *Mat. Res. Soc. Symp. Proc.* **757**, 565 (2003).
88. Vitorge, P., Capdevila, H.: Thermodynamic data for modelling actinide speciation in environmental waters. *Radiochim. Acta* **91**, 623 (2003).
89. Guillaumont, R., Adloff, J. P.: Behaviour of environmental plutonium at very low concentration. *Radiochim. Acta* **58/59**, 53 (1992).
90. Vitorge, P.: *Chimie des actinides*. Techniques de l'ingénieur 630 (1999).
91. Tipping, E.: Modelling the binding of europium and the actinides by humic substances. *Radiochim. Acta* **62**, 141 (1993).
92. Santschi, P. H., Roberts, K. A., Guo, L. D.: Organic nature of colloidal actinides transported in surface water environments. *Environ. Sci. Technol.* **36**, 3711 (2002).
93. Cantrell, K. J.: Actinide (III) carbonate complexation. *Polyhedron* **7**, 573 (1988).
94. Silva, R. J., Bidoglio, G., Rand, M., Robouch, P., Wanner, H., Puigdomènech, I.: *Chemical thermodynamics of americium with an appendix on Chemical thermodynamics of uranium (Grenthe, I., Sandino, M.C.A., Puigdomenech, I., Rand, M.H.)*. North Holland, Amsterdam (1995).

95. Aguer, J. P., Richard, C., Andreux, F.: Effect of light on humic acid substances: production of reactive species. *Analisis* **27**, 387 (1999).
96. Schild, D., Marquardt, C., Seibert, A. Analysis of Pu-Humate by XPS. 9<sup>th</sup> International Conference on Chemistry and Migration Behavior of Actinides and Fission Products in the Geosphere, Migration '03. September 21-26, 2003, Gyeongju, Korea (2003).
97. Artinger, R., Denecke, M. A., Kuczewski, B., Marquardt, C., Schild, D., Seibert, A., Fanghänel, T. Redox behaviour of Pu ions in a natural ground water rich in humic substances. 9<sup>th</sup> International Conference on Chemistry and Migration Behavior of Actinides and Fission Products in the Geosphere, Migration '03. September 21-26, 2003, Gyeongju, Korea (2003).
98. Zauzig, J., Stepniewski, W., Horn, R.: Oxygen concentration and redox potential gradient in unsaturated model soil aggregates. *Soil Sci. Soc. Am. J.* **57**, 908 (1993).
99. Matthiessen, A.: Evaluating the redox capacity and the redox potential of humic acids by redox titrations. In: *Humic substances in the global environment and implications on human health* (Senesi, N. and Miano, T. M. eds.). Elsevier, (1994) p. 187.
100. Struyk, Z., Sposito, G.: Redox properties of standard humic acids. *Geoderma* **102**, 329 (2001).
101. Laszak, I.: Étude des interactions entre colloïdes naturels et éléments radiotoxiques par spectrofluorimétrie laser à résolution temporelle. étude chimique et spectroscopique. Université Pierre et Marie Curie - Paris VI, Paris (1997).
102. Li, W. C., Victor, D. M., Chakrabarti, C. L.: Effect of pH and uranium concentration on interaction of uranium(VI) and uranium(IV) with organic ligands in aqueous solutions. *Anal. Chem.* **52**, 523 (1980).
103. Kim, J. I.: Actinide colloids in natural aquifer systems. *Material Research Society Bulletin* **Dec 1994**, 47 (1994).
104. Cromières, L., Moulin, V., Fourest, B., Guillaumont, R., Giffaut, E.: Sorption of thorium onto hematite colloids. *Radiochim. Acta* **82**, 249 (1998).
105. Reiller, P., Moulin, V., Casanova, F., Dautel, C.: Retention behaviour of humic substances onto mineral surfaces and consequences upon thorium (IV) mobility: case of iron oxides. *Appl. Geochem.* **17**, 1551 (2002).
106. Asbury, S. M. L., Lamont, S. P., Clark, S. B.: Plutonium partitioning to colloidal and particulate matter in an acidic, sandy sediment: Implications for remediation alternatives and plutonium migration. *Environ. Sci. Technol.* **35**, 2295 (2001).
107. Tipping, E., Higgins, D. C.: The effect of adsorbed humic substances on the colloid stability of haematite particles. *Colloids and Surfaces* **5**, 85 (1982).
108. Ledin, A., Karlsson, S., Allard, B.: Effects of pH, ionic strength and a fulvic acid in size distribution and surface charge of colloidal quartz and hematite. *Appl. Geochem.* **8**, 409 (1993).
109. Kretzschmar, R., Sticher, H.: Transport of humic-coated iron oxide colloids in a sandy soil: Influence of Ca<sup>2+</sup> and trace metals. *Environ. Sci. Technol.* **31**, 3497 (1997).
110. Vermeer, A. W. P., McCulloch, J. K., van Riemsdijk, W. H., L.K., K.: Metal ion adsorption to complexes of humic acid and metal oxides: deviation from the additivity rule. *Environ. Sci. Technol.* **33**, 3892 (1999).

## Figure Caption

Figure 1: Speciation of thorium (IV) vs. pH taking into account  $\text{ThHA}(\text{IV})$  ( $\log \beta_{1,\text{IV}} = 12.4$  referring to [61]:  $[\text{Th}] = 10^{-10} \text{ m}$ ,  $[\text{NaClO}_4] = 0.101 \text{ m}$ ,  $(\text{HA}) = 140 \text{ mg/L}$  or  $[\text{HA}(\text{IV})] = 1.85 \cdot 10^{-5} \text{ eq/L}$ ; initial experimental data from [50].

Figure 2: Determination of  $\log \beta_{1,3,\text{I}}$  (Eq. 14) and  $\log \beta_{1,4,\text{I}}$  (Eq. 16) from experimental data in [51], referring to auxiliary data in [61] (see Table 3).

Figure 3: Speciation of thorium (IV) vs. pH taking into account  $\text{ThHA}(\text{IV})$  ( $\log \beta_{1,\text{IV}} = 12.4$  from experimental data in [50]) and  $\text{Th}(\text{OH})_3\text{HA}(\text{I})$  ( $\log \beta_{1,3,\text{I}} = 35.1$  from experimental data in [51]) referring to auxiliary data in [61]: a.  $[\text{NaClO}_4] = 0.101 \text{ m}$ ,  $[\text{HA}(\text{I})] = 7.8 \cdot 10^{-4} \text{ eq/L}$ ,  $[\text{HA}(\text{IV})]_{\text{T}} = 1.95 \cdot 10^{-4} \text{ eq/L}$ ; b.  $[\text{NaClO}_4] = 0.101 \text{ m}$ ,  $[\text{HA}(\text{I})] = 1.48 \cdot 10^{-6} \text{ eq/L}$ ,  $[\text{HA}(\text{IV})] = 3.7 \cdot 10^{-7} \text{ eq/L}$ .

Figure 4: Speciation of thorium (IV) vs. pH taking into account  $\text{Th}(\text{OH})_4\text{HA}(\text{I})$  with  $\log \beta_{1,4,\text{I}} = 41.6$  referring to [61]: a.  $[\text{NaClO}_4] = 0.101 \text{ m}$ ,  $[\text{HA}(\text{I})] = 7.8 \cdot 10^{-4} \text{ eq/L}$ ,  $[\text{HA}(\text{IV})] = 1.95 \cdot 10^{-4} \text{ eq/L}$ ; b.  $[\text{NaClO}_4] = 0.101 \text{ m}$ ,  $[\text{HA}(\text{I})] = 1.48 \cdot 10^{-6} \text{ eq/L}$ ,  $[\text{HA}(\text{IV})] = 0.3 \cdot 10^{-6} \text{ eq/L}$ .

Figure 5: Calculated solubility of  $\text{ThO}_2(\text{cr})$   $[\text{NaClO}_4] = 0.101 \text{ m}$  using  $\text{ThHA}(\text{IV})$  ( $\log \beta_{1,\text{IV}} = 12.4$ ) and  $\text{Th}(\text{OH})_4\text{HA}(\text{I})$  ( $\log \beta_{1,4,\text{I}} = 41.6$ ), referring to auxiliary data in [61]; plain line  $[\text{HA}]_{\text{T}} = 0 \text{ eq/L}$ , dashed line  $[\text{HA}]_{\text{T}} = 7.4 \cdot 10^{-4} \text{ eq/L}$  ( $\text{HA} = 140 \text{ mg/L}$ ).

Figure 6: Speciation of thorium (IV) vs. pH referring to [57, 58],  $\log \beta_{1,\text{IV}} = 12.4$ ,  $[\text{NaClO}_4] = 0.101 \text{ m}$ ,  $[\text{TIC}] = 8.2 \cdot 10^{-3} \text{ m}$ ,  $[\text{HA}(\text{I})] = 7.8 \cdot 10^{-4} \text{ eq/L}$ ,  $[\text{HA}(\text{IV})]_{\text{T}} = 1.9 \cdot 10^{-4} \text{ eq/L}$ ;  $\log \beta_{1,\text{IV}} = 12.4$ ; a.  $\log \beta_{1,3,\text{IV}} = 38.7$ ; b.  $\log \beta_{1,4,\text{IV}} = 45.2$ ; c.  $(\text{HA}) = 0.6 \text{ mg/L}$ ,  $\text{PEC} = 5.4 \cdot 10^{-3}$ ,  $[\text{HA}(\text{I})] = 3.23 \cdot 10^{-6} \text{ eq/L}$ ,  $[\text{HA}(\text{IV})] = 1.08 \cdot 10^{-6} \text{ eq/L}$ .

Figure 7: Speciation of plutonium vs. pH referring to [81],  $\log \beta_{1,4,\text{IV}} = 52$ ,  $E_{\text{H}} - 30 \text{ mV/SHE}$ ,  $[\text{TIC}] = 8.2 \cdot 10^{-3} \text{ m}$ ,  $[\text{HA}]_{\text{T}} = 5.4 \cdot 10^{-4} \text{ eq/L}$ .

Figure 8: Speciation of neptunium vs. pH referring to [81],  $\log \beta_{1,4,\text{IV}} = 49.3$ ,  $E_{\text{H}} - 30 \text{ mV/SHE}$ ,  $[\text{TIC}] = 8.2 \cdot 10^{-3} \text{ m}$ ,  $[\text{HA}]_{\text{T}} = 5.4 \cdot 10^{-4} \text{ eq/L}$ .

Figure 9: Speciation of uranium vs. pH referring to [71, 94],  $\log \beta_{1,4,\text{IV}} = 54.4$ ,  $E_{\text{H}} - 30 \text{ mV/SHE}$ ,  $[\text{TIC}] = 8.23 \cdot 10^{-3} \text{ m}$ ,  $[\text{HA}]_{\text{T}} = 5.4 \cdot 10^{-4} \text{ eq/L}$ .

Figure 10: Speciation of actinides  $10^{-10} \text{ m}$  vs.  $E_{\text{H}}$  (V/SHE),  $\text{pH} = 7$ ,  $[\text{NaClO}_4] = 0.101 \text{ m}$ ,  $[\text{TIC}] = 8.2 \cdot 10^{-3} \text{ m}$  and  $[\text{HA}]_{\text{T}} = 5.4 \cdot 10^{-4} \text{ eq/L}$ ; a. neptunium; b. plutonium; c. uranium.

Figure 11:  $E_{\text{H}}$ -pH diagrams for a.) neptunium, b.) plutonium and c.) uranium species drawn with data from Table 2 for inorganic complexes and Table 4 for humic complexes. Redox properties of HS are not taken into account;  $[\text{M}] = 10^{-10} \text{ m}$ , total carbonate =  $8.2 \cdot 10^{-3} \text{ m}$ ,  $(\text{HA}) = 100 \text{ mg/L}$ ,  $\text{PEC} = 5.4 \text{ meq/g}$ ,  $[\text{NaClO}_4] = 0.101 \text{ m}$ .

## Table Caption

**Table 1: Estimation of  $\log \beta_{1..IV}$  using CNM, from experimental data in Nash and Choppin [50].**

**Table 2: Complexation constant used in this study. Extrapolation at 0.101 *m* NaClO<sub>4</sub> with SIT [71], using the parameters stated in the reference.**

**Table 3: Estimation of the stability constants for Th(OH)<sub>3</sub>HA(*l*) and Th(OH)<sub>4</sub>HA(*l*) from experimental data in [51] referring to [61]. Uncertainties are 95% confidence interval.<sup>a</sup>**

**Table 4: Stability constants for humic complexes used in this study. The constants that take into account the reduction of M(VI) are calculated using the data from Table 2.**

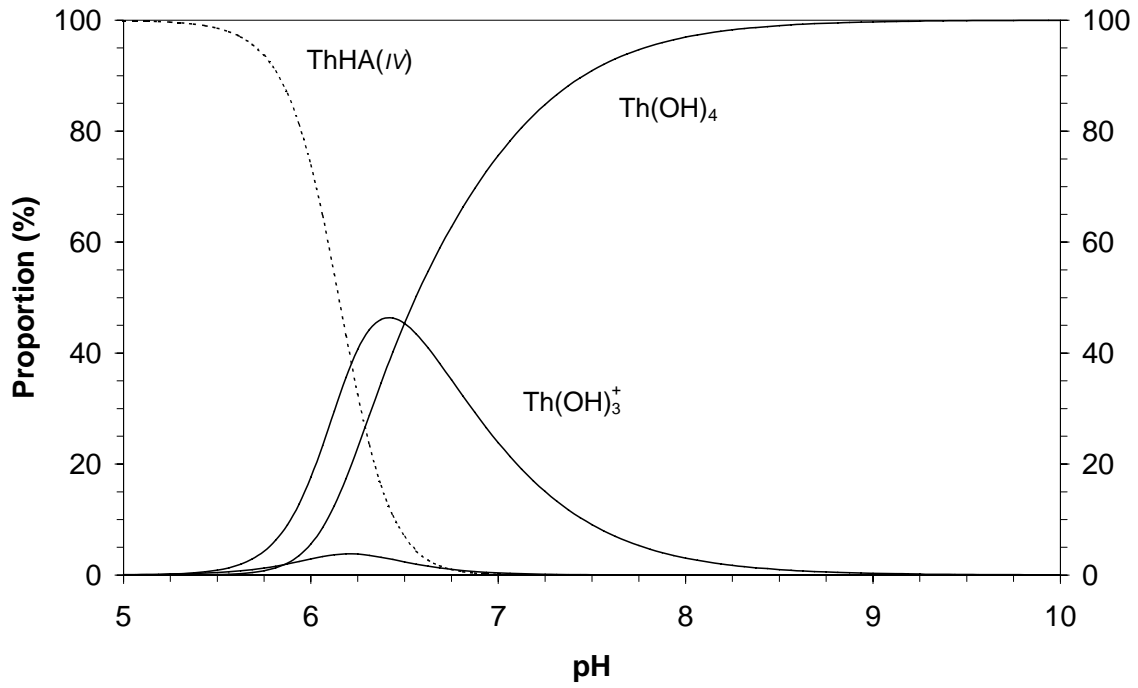


Figure 1: Speciation of thorium (IV) vs. pH taking into account  $\text{ThHA(IV)}$   $\log \beta_{1,IV} = 12.4$  referring to [61]:  $[\text{Th}] = 10^{-10} \text{ m}$ ,  $[\text{NaClO}_4] = 0.101 \text{ m}$ ,  $(\text{HA}) = 140 \text{ mg/L}$  or  $[\text{HA(IV)}] = 1.85 \cdot 10^{-5} \text{ eq/L}$ ; initial experimental data from [50].

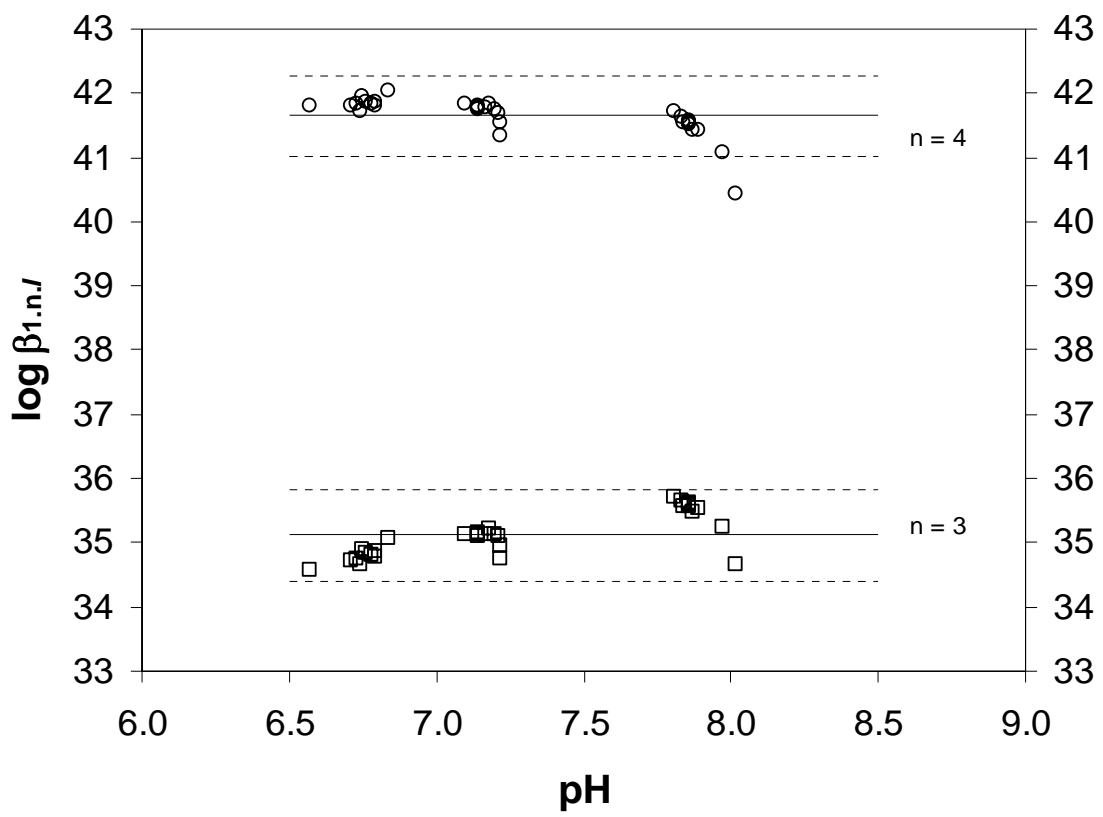


Figure 2: Determination of  $\log \beta_{1,3,l}$  (Eq. 14) and  $\log \beta_{1,4,l}$  (Eq. 16) from experimental data in [51], referring to auxiliary data in [61] (see Table 3).

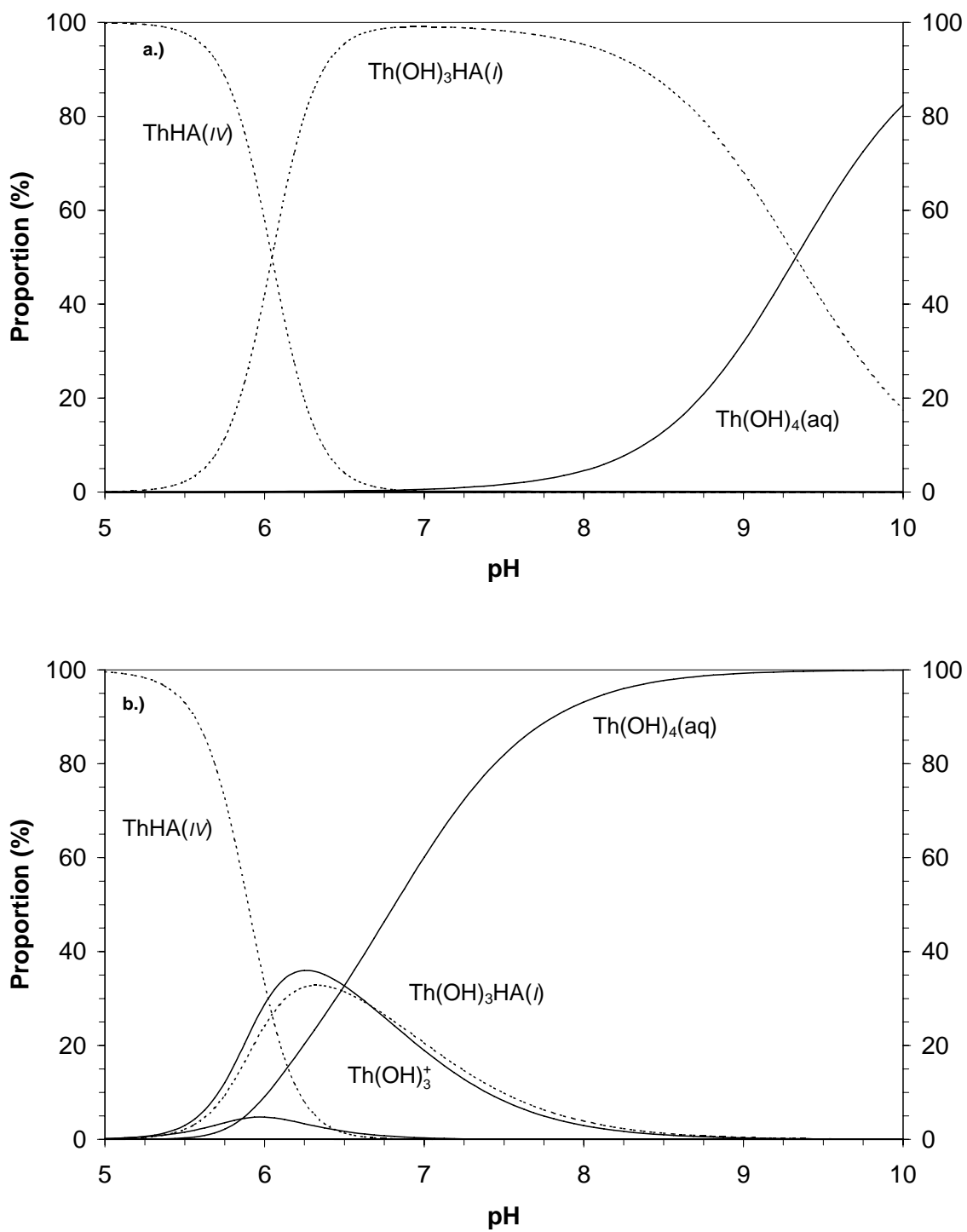


Figure 3: Speciation of thorium (IV) vs. pH taking into account  $\text{ThHA}(IV)$  ( $\log \beta_{1,IV} = 12.4$  from experimental data in [50]) and  $\text{Th}(\text{OH})_3\text{HA}(I)$  ( $\log \beta_{1,3,I} = 35.1$  from experimental data in [51]) referring to auxiliary data in [61]: a.  $[\text{NaClO}_4] = 0.101 \text{ m}$ ,  $[\text{HA}(I)] = 7.8 \cdot 10^{-4} \text{ eq/L}$ ,  $[\text{HA}(IV)]_T = 1.95 \cdot 10^{-4} \text{ eq/L}$ ; b.  $[\text{NaClO}_4] = 0.101 \text{ m}$ ,  $[\text{HA}(I)] = 1.48 \cdot 10^{-6} \text{ eq/L}$ ,  $[\text{HA}(IV)] = 3.7 \cdot 10^{-7} \text{ eq/L}$ .

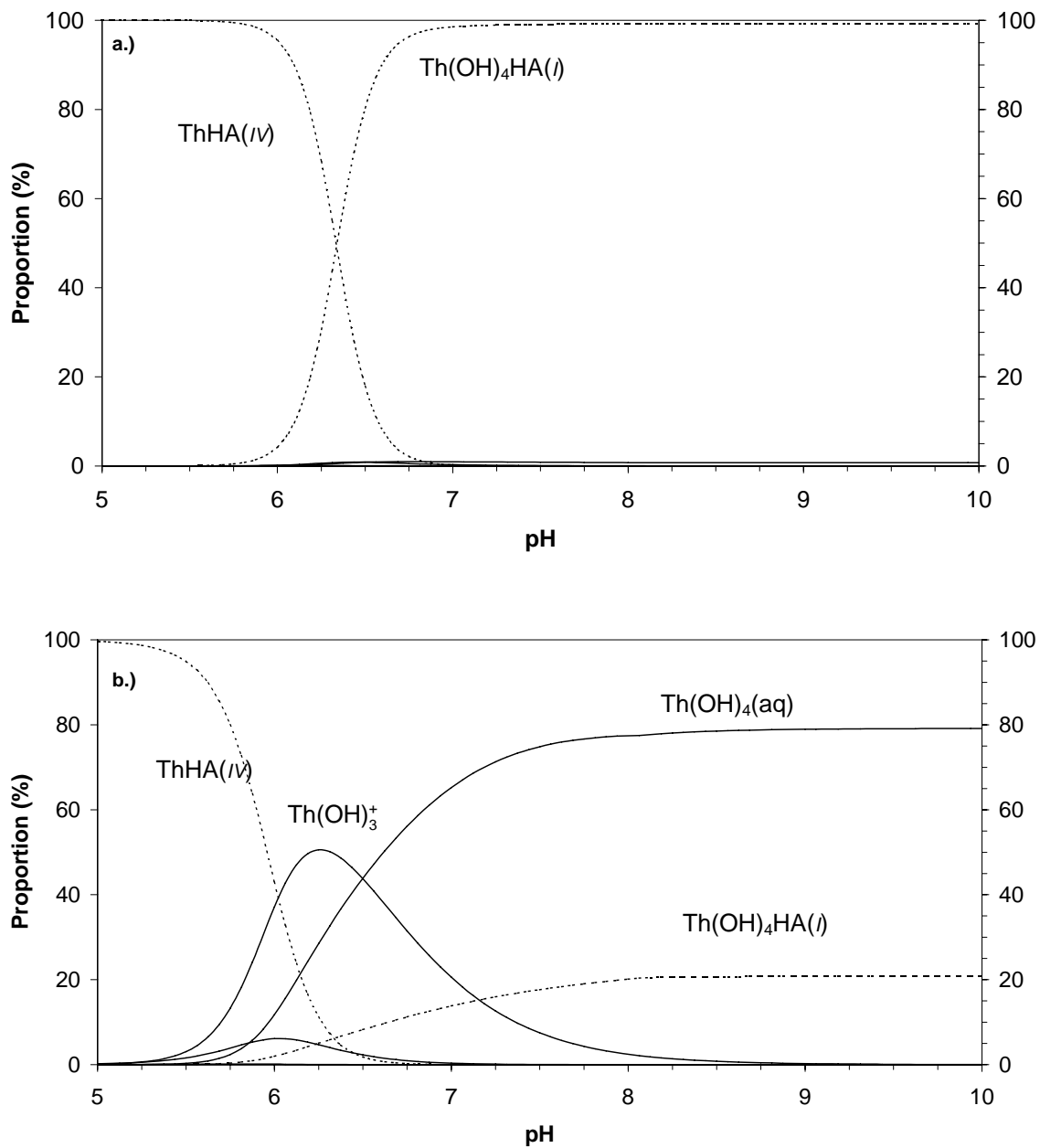


Figure 4: Speciation of thorium (IV) vs. pH taking into account  $\text{Th}(\text{OH})_4\text{HA}(\text{l})$  with  $\log \beta_{1,4,1} = 41.6$  referring to [61]: a.  $[\text{NaClO}_4] = 0.101 \text{ m}$ ,  $[\text{HA}(\text{l})] = 7.8 \cdot 10^{-4} \text{ eq/L}$ ,  $[\text{HA}(\text{IV})] = 1.95 \cdot 10^{-4} \text{ eq/L}$ ; b.  $[\text{NaClO}_4] = 0.101 \text{ m}$ ,  $[\text{HA}(\text{l})] = 1.48 \cdot 10^{-6} \text{ eq/L}$ ,  $[\text{HA}(\text{IV})] = 0.3 \cdot 10^{-6} \text{ eq/L}$ .

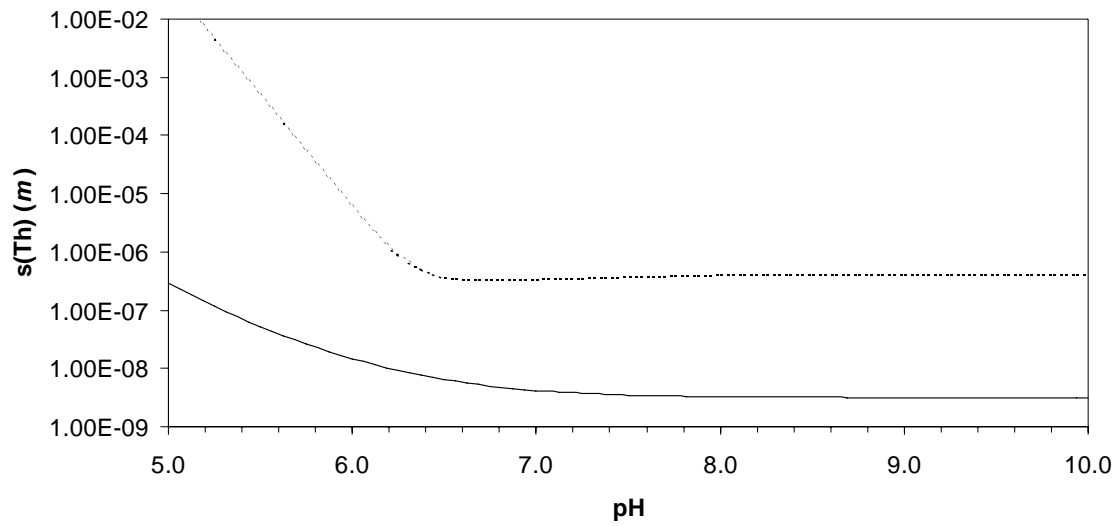


Figure 5: Calculated solubility of  $\text{ThO}_2(\text{cr})$   $[\text{NaClO}_4] = 0.101 \text{ m}$  using  $\text{ThHA}(\text{IV})$  ( $\log \beta_{1,\text{IV}} = 12.4$ ) and  $\text{Th}(\text{OH})_4\text{HA}(\text{I})$  ( $\log \beta_{1,4,\text{I}} = 41.6$ ), referring to auxiliary data in [61]; plain line  $[\text{HA}]_{\text{T}} = 0 \text{ eq/L}$ , dashed line  $[\text{HA}]_{\text{T}} = 7.4 \cdot 10^{-4} \text{ eq/L}$  ( $\text{HA} = 140 \text{ mg/L}$ ).

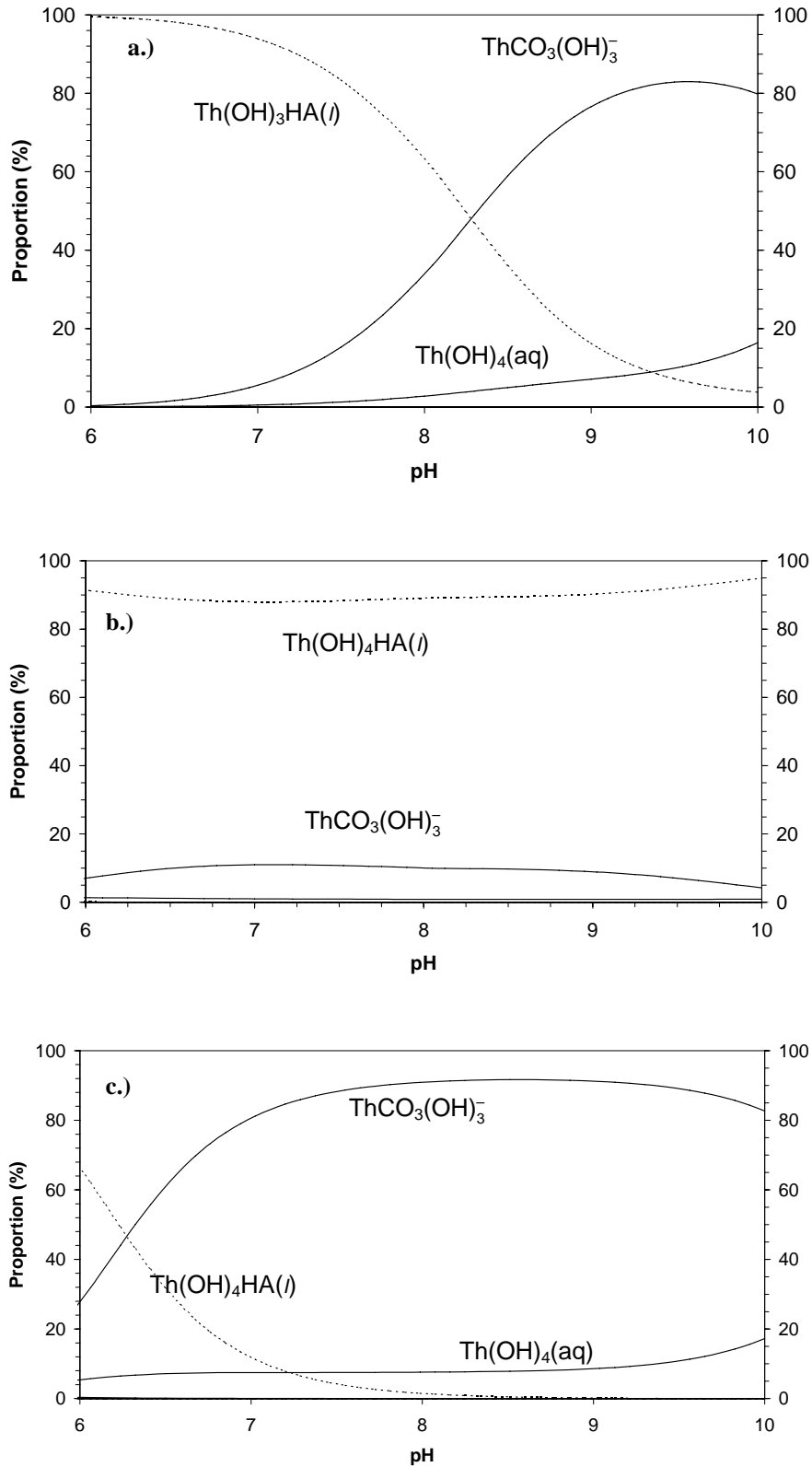


Figure 6: Speciation of thorium (IV) vs. pH referring to [57, 58],  $\log \beta_{1.IV} = 12.4$ ,  $[\text{NaClO}_4] = 0.101 \text{ m}$ ,  $[\text{TIC}] = 8.2 \cdot 10^{-3} \text{ m}$ ,  $[\text{HA}(l)] = 7.8 \cdot 10^{-4} \text{ eq/L}$ ,  $[\text{HA}(l)]_T = 1.9 \cdot 10^{-4} \text{ eq/L}$ ;  $\log \beta_{1.IV} = 12.4$ ; a.  $\log \beta_{1.3.IV} = 38.7$ ; b.  $\log \beta_{1.4.IV} = 45.2$ ; c.  $(\text{HA}) = 0.6 \text{ mg/L}$ ,  $\text{PEC} = 5.4 \cdot 10^{-3}$ ,  $[\text{HA}(l)] = 3.23 \cdot 10^{-6} \text{ eq/L}$ ,  $[\text{HA}(l)] = 1.08 \cdot 10^{-6} \text{ eq/L}$ .

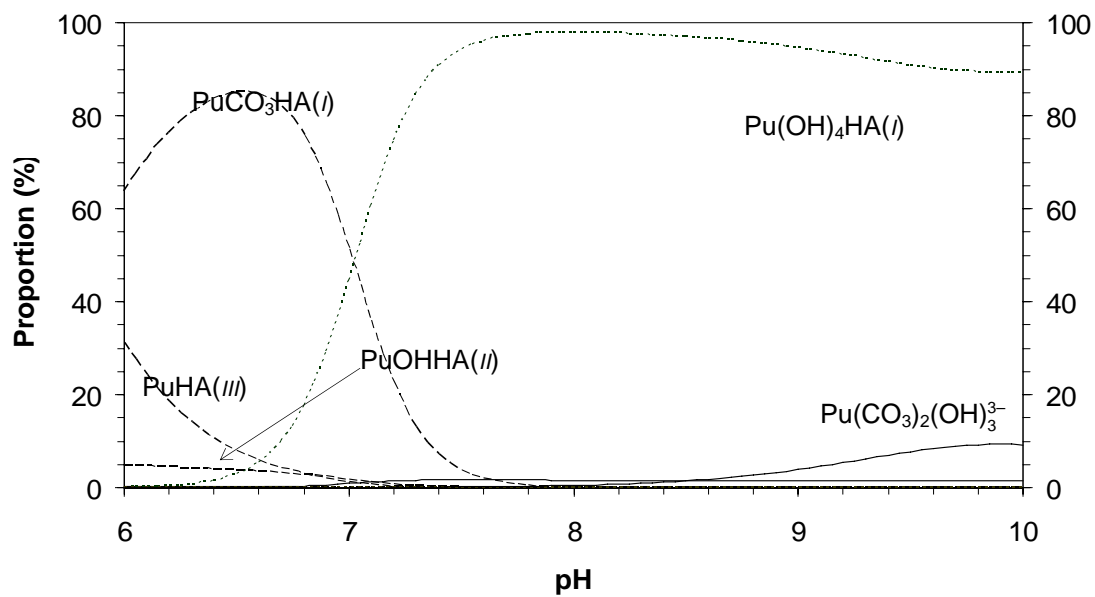


Figure 7: Speciation of plutonium vs. pH referring to [81],  $\log \beta_{1.4,IV} = 52$ ,  $E_H = -30$  mV/SHE,  $[TIC] = 8.2 \cdot 10^{-3}$  m,  $[HA]_T = 5.4 \cdot 10^{-4}$  eq/L.

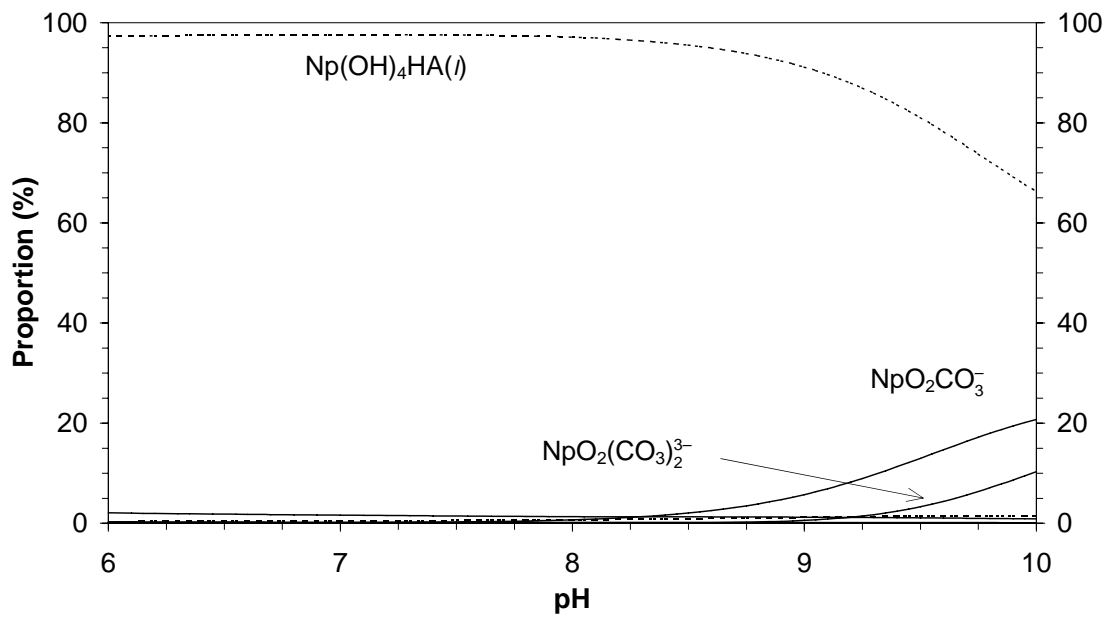


Figure 8: Speciation of neptunium vs. pH referring to [81],  $\log \beta_{1.4,IV} = 49.3$ ,  $E_H = -30$  mV/SHE,  $[\text{TIC}] = 8.2 \cdot 10^{-3}$  m,  $[\text{HA}]_T = 5.4 \cdot 10^{-4}$  eq/L

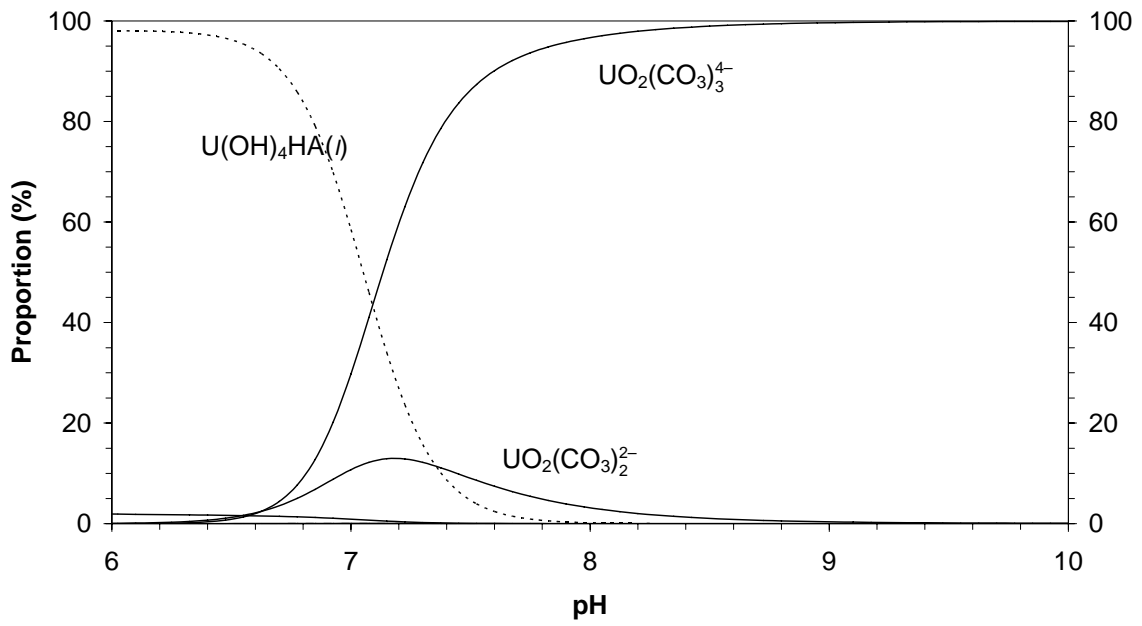


Figure 9: Speciation of uranium vs. pH referring to [71, 94],  $\log \beta_{1.4,IV} = 54.4$ ,  $E_H = -30$  mV/SHE,  $[TIC] = 8.23 \cdot 10^{-3}$  m,  $[HA]_T = 5.4 \cdot 10^{-4}$  eq/L.

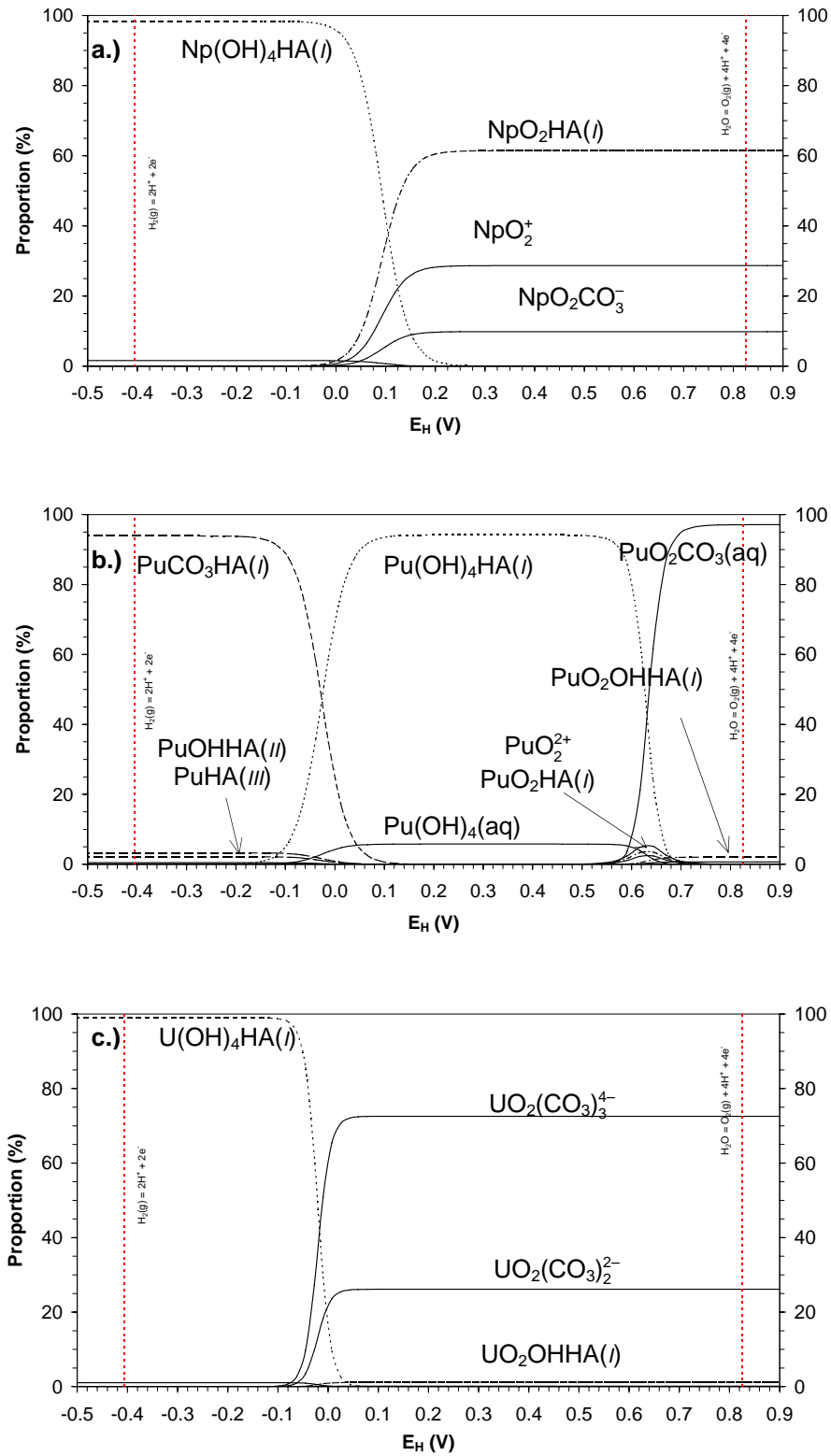


Figure 10: Speciation of actinides  $10^{-10}$  m vs.  $E_H$  (V/SHE), pH = 7,  $[\text{NaClO}_4] = 0.101$  m,  $[\text{TIC}] = 8.2 \cdot 10^{-3}$  m and  $[\text{HA}]_T = 5.4 \cdot 10^{-4}$  eq/L; a. neptunium; b. plutonium; c. uranium.

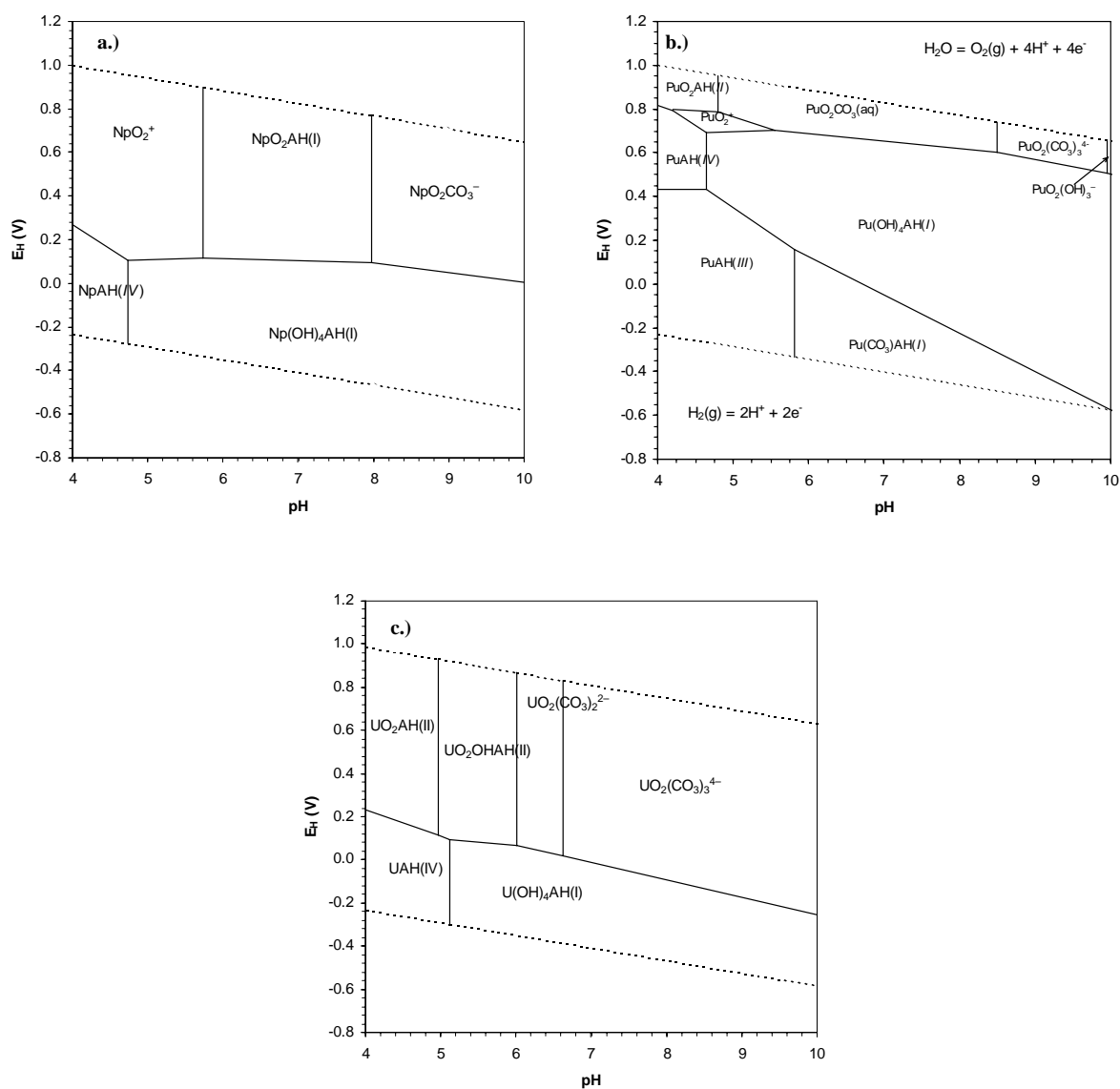


Figure 11:  $E_h$ -pH diagrams for a.) neptunium, b.) plutonium and c.) uranium species drawn with data from Table 2 for inorganic complexes and Table 4 for humic complexes. Redox properties of HS are not taken into account;  $[M] = 10^{-10} m$ , total carbonate =  $8.2 \cdot 10^{-3} m$ , (HA) = 100 mg/L, PEC = 5.4 meq/g,  $[\text{NaClO}_4] = 0.101 m$ .

**Table 1: Estimation of  $\log \beta_{1,IV}$  using CNM, from experimental data in Nash and Choppin [50].**

pH	D	[HA] <sub>T</sub>	[HA(IV)]	[AcO <sup>-</sup> ]	$\alpha$	$\frac{D^{\circ}}{D} - 1$	$\beta_{1,IV} \times LC$	$\log(\beta_{1,IV} \times LC)$
3.98	31.48			$1.16 \cdot 10^{-2}$	$9.46 \cdot 10^3$			
3.98	33.75							
3.937	2.170	$1.48 \cdot 10^{-6}$	$3.58 \cdot 10^{-7}$	$1.07 \cdot 10^{-2}$	$7.60 \cdot 10^3$	13.51	$2.87 \cdot 10^{11}$	11.46
3.937	2.195					14.38	$3.05 \cdot 10^{11}$	11.48
3.939	1.446	$1.98 \cdot 10^{-6}$	$4.77 \cdot 10^{-7}$	$1.08 \cdot 10^{-2}$	$7.68 \cdot 10^3$	20.77	$3.34 \cdot 10^{11}$	11.52
3.939	1.423					22.71	$3.65 \cdot 10^{11}$	11.56
3.93	1.120	$2.47 \cdot 10^{-6}$	$5.97 \cdot 10^{-7}$	$1.06 \cdot 10^{-2}$	$7.34 \cdot 10^3$	27.11	$3.33 \cdot 10^{11}$	11.52
3.93	1.086					30.08	$3.70 \cdot 10^{11}$	11.57
3.961	0.362	$4.95 \cdot 10^{-6}$	$1.20 \cdot 10^{-6}$	$1.12 \cdot 10^{-2}$	$8.59 \cdot 10^3$	85.91	$6.17 \cdot 10^{11}$	11.79
3.961	0.380					87.90	$6.31 \cdot 10^{11}$	11.80
3.928	0.219	$7.38 \cdot 10^{-6}$	$1.78 \cdot 10^{-6}$	$1.06 \cdot 10^{-2}$	$7.26 \cdot 10^3$	142.42	$5.80 \cdot 10^{11}$	11.76
3.928	0.218					154.06	$6.28 \cdot 10^{11}$	11.80
3.922	0.147	$9.88 \cdot 10^{-6}$	$2.39 \cdot 10^{-6}$	$1.05 \cdot 10^{-2}$	$7.04 \cdot 10^3$	212.61	$6.27 \cdot 10^{11}$	11.80
3.922	0.155					217.07	$6.40 \cdot 10^{11}$	11.81
							$\log(\overline{\beta_{1,IV} \times LC}) \pm S_{95\%} = 11.7 \pm 0.3$	

**Table 2: Complexation constant used in this study. Extrapolation at 0.101 m NaClO<sub>4</sub> with SIT [71], using the parameters stated in the reference.**

Equilibrium	log K [71]	Th	U [71, 94]	Np [81]	Pu [81]
CO <sub>2</sub> (aq) + H <sub>2</sub> O ⇌ HCO <sub>3</sub> <sup>-</sup> + H <sup>+</sup>	-6.15				
HCO <sub>3</sub> <sup>-</sup> ⇌ CO <sub>3</sub> <sup>2-</sup> + H <sup>+</sup>	-9.90				
H <sub>2</sub> O ⇌ H <sup>+</sup> + OH <sup>-</sup>	-13.80				
M <sup>3+</sup> + H <sub>2</sub> O ⇌ MOH <sup>2+</sup> + H <sup>+</sup>				-7.24	-7.34
M <sup>3+</sup> + 2H <sub>2</sub> O ⇌ M(OH) <sub>2</sub> <sup>+</sup> + 2H <sup>+</sup>					-15.66
M <sup>3+</sup> + CO <sub>3</sub> <sup>2-</sup> ⇌ MCO <sub>3</sub> <sup>+</sup>					6.21 [81, 93]
M <sup>3+</sup> + 2CO <sub>3</sub> <sup>2-</sup> ⇌ M(CO <sub>3</sub> ) <sub>2</sub> <sup>-</sup>					10.69 [81, 93]
		[62]			
M <sup>4+</sup> + AcO <sup>-</sup> ⇌ MOAc <sup>3+</sup>		4.04			
M <sup>4+</sup> + 2AcO <sup>-</sup> ⇌ M(OAc) <sub>2</sub> <sup>2+</sup>		7.33			
M <sup>4+</sup> + 3AcO <sup>-</sup> ⇌ M(OAc) <sub>3</sub> <sup>+</sup>		9.47			
M <sup>4+</sup> + 4AcO <sup>-</sup> ⇌ M(OAc) <sub>4</sub>		11.00			
		[61] [57, 58]			
M <sup>4+</sup> + H <sub>2</sub> O ⇌ MOH <sup>3+</sup> + H <sup>+</sup>		-2.85 -3.79	-1.18	-0.93	-1.45
M <sup>4+</sup> + 2H <sub>2</sub> O ⇌ M(OH) <sub>2</sub> <sup>2+</sup> + 2H <sup>+</sup>		-7.08			
M <sup>4+</sup> + 3H <sub>2</sub> O ⇌ M(OH) <sub>3</sub> <sup>+</sup> + 3H <sup>+</sup>		-12.30 -10.38			
M <sup>4+</sup> + 4H <sub>2</sub> O ⇌ M(OH) <sub>4</sub> + 4H <sup>+</sup>		-18.80 -15.16	-6.00	-11.09	-8.27
M <sup>4+</sup> + 5CO <sub>3</sub> <sup>2-</sup> ⇌ M(CO <sub>3</sub> ) <sub>5</sub> <sup>6-</sup>		32.27	33.94	35.58	34.07
M <sup>4+</sup> + CO <sub>3</sub> <sup>2-</sup> + 3H <sub>2</sub> O ⇌ MCO <sub>3</sub> (OH) <sub>3</sub> <sup>-</sup> + 3H <sup>+</sup>		-2.18			
M <sup>4+</sup> + 2CO <sub>3</sub> <sup>2-</sup> + 3H <sub>2</sub> O ⇌ M(CO <sub>3</sub> ) <sub>2</sub> (OH) <sub>3</sub> <sup>3-</sup> + 3H <sup>+</sup>					7.22 [88]
MO <sub>2</sub> <sup>+</sup> + H <sub>2</sub> O ⇌ MO <sub>2</sub> OH + H <sup>+</sup>				-11.29	-9.72
MO <sub>2</sub> <sup>+</sup> + CO <sub>3</sub> <sup>2-</sup> ⇌ MO <sub>2</sub> CO <sub>3</sub> <sup>-</sup>				4.58	4.72
MO <sub>2</sub> <sup>+</sup> + 2CO <sub>3</sub> <sup>2-</sup> ⇌ MO <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> <sup>3-</sup>				6.61	6.39
MO <sub>2</sub> <sup>2+</sup> + H <sub>2</sub> O ⇌ MO <sub>2</sub> OH <sup>+</sup> + H <sup>+</sup>			-5.38		-5.71
MO <sub>2</sub> <sup>2+</sup> + 2H <sub>2</sub> O ⇌ MO <sub>2</sub> (OH) <sub>2</sub> + 2H <sup>+</sup>			-10.53		-13.40
MO <sub>2</sub> <sup>2+</sup> + 3H <sub>2</sub> O ⇌ MO <sub>2</sub> (OH) <sub>3</sub> + 3H <sup>+</sup>			-19.19		-19.19 [88]
MO <sub>2</sub> <sup>2+</sup> + CO <sub>3</sub> <sup>2-</sup> ⇌ MO <sub>2</sub> CO <sub>3</sub>			8.80		10.76
MO <sub>2</sub> <sup>2+</sup> + 2CO <sub>3</sub> <sup>2-</sup> ⇌ MO <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> <sup>2-</sup>			16.16		13.66
MO <sub>2</sub> <sup>2+</sup> + 3CO <sub>3</sub> <sup>2-</sup> ⇌ MO <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> <sup>4-</sup>			21.66		17.76
MO <sub>2</sub> <sup>+</sup> + ½ H <sub>2</sub> + 4H <sup>+</sup> ⇌ M <sup>4+</sup> + 2H <sub>2</sub> O + H <sup>+</sup>				11.41	
MO <sub>2</sub> <sup>+</sup> + H <sub>2</sub> (g) + 4H <sup>+</sup> ⇌ M <sup>3+</sup> + 2H <sub>2</sub> O + 2H <sup>+</sup>				14.14	
MO <sub>2</sub> <sup>2+</sup> + ½ H <sub>2</sub> ⇌ MO <sub>2</sub> <sup>+</sup> + H <sup>+</sup>					15.52
MO <sub>2</sub> <sup>2+</sup> + H <sub>2</sub> + 4H <sup>+</sup> ⇌ M <sup>4+</sup> + 2H <sub>2</sub> O + 2H <sup>+</sup>			9.94		34.13
MO <sub>2</sub> <sup>2+</sup> + 3/2 H <sub>2</sub> + 4H <sup>+</sup> ⇌ M <sup>3+</sup> + 2H <sub>2</sub> O + 3H <sup>+</sup>					51.12

Following the recommendation in [71], H<sup>+</sup> issued from the hydrogen oxidation are not taken into account in Δz<sup>2</sup> and Δε, and are thus written in italic.

**Table 3: Estimation of the stability constants for Th(OH)<sub>3</sub>HA(l) and Th(OH)<sub>4</sub>HA(l) from experimental data in [51] referring to [61]. Uncertainties are 95% confidence interval.<sup>a</sup>**

pH	[HA(l)]	R(%)	K <sub>d</sub>	α	log β <sub>1.3,l</sub>	log β <sub>1.4,l</sub>
7.91	0	0.857	2.395 10 <sup>4</sup>			
8.02	1.14 10 <sup>-5</sup>	0.842	2.133 10 <sup>4</sup>	1.97 10 <sup>13</sup>	34.7	40.4
7.97	2.27 10 <sup>-5</sup>	0.744	1.165 10 <sup>4</sup>	1.25 10 <sup>13</sup>	35.3	41.1
7.87	3.41 10 <sup>-5</sup>	0.578	5.469 10 <sup>3</sup>	5.00 10 <sup>12</sup>	35.5	41.4
7.89	4.55 10 <sup>-5</sup>	0.511	4.184 10 <sup>3</sup>	6.00 10 <sup>12</sup>	35.5	41.4
7.86	5.68 10 <sup>-5</sup>	0.430	3.012 10 <sup>3</sup>	4.57 10 <sup>12</sup>	35.6	41.5
7.86	6.54 10 <sup>-5</sup>	0.368	2.331 10 <sup>3</sup>	4.57 10 <sup>12</sup>	35.6	41.6
7.86	7.67 10 <sup>-5</sup>	0.347	2.122 10 <sup>3</sup>	4.57 10 <sup>12</sup>	35.6	41.5
7.84	8.53 10 <sup>-5</sup>	0.332	1.986 10 <sup>3</sup>	3.81 10 <sup>12</sup>	35.6	41.5
7.81	1.14 10 <sup>-4</sup>	0.207	1.042 10 <sup>3</sup>	2.90 10 <sup>12</sup>	35.7	41.7
7.83	1.71 10 <sup>-4</sup>	0.176	8.549 10 <sup>2</sup>	3.47 10 <sup>12</sup>	35.7	41.6
					35.5 ± 0.7	41.4 ± 0.8
7.31	0	0.756	1.243 10 <sup>4</sup>			
7.22	1.14 10 <sup>-5</sup>	0.630	6.825 10 <sup>3</sup>	1.44 10 <sup>10</sup>	34.8	41.3
7.20	2.27 10 <sup>-5</sup>	0.377	2.420 10 <sup>3</sup>	1.20 10 <sup>10</sup>	35.1	41.7
7.14	3.41 10 <sup>-5</sup>	0.298	1.698 10 <sup>3</sup>	7.10 10 <sup>9</sup>	35.1	41.8
7.17	4.55 10 <sup>-5</sup>	0.242	1.279 10 <sup>3</sup>	9.24 10 <sup>9</sup>	35.1	41.8
7.18	5.68 10 <sup>-5</sup>	0.187	9.221 10 <sup>2</sup>	1.01 10 <sup>10</sup>	35.2	41.8
7.14	6.54 10 <sup>-5</sup>	0.182	8.920 10 <sup>2</sup>	7.10 10 <sup>9</sup>	35.1	41.8
7.10	7.67 10 <sup>-5</sup>	0.149	7.012 10 <sup>2</sup>	5.00 10 <sup>9</sup>	35.1	41.8
7.14	8.53 10 <sup>-5</sup>	0.140	6.513 10 <sup>2</sup>	7.10 10 <sup>9</sup>	35.2	41.8
7.21	1.14 10 <sup>-4</sup>	0.137	6.348 10 <sup>2</sup>	1.31 10 <sup>10</sup>	35.1	41.7
7.22	1.71 10 <sup>-4</sup>	0.129	5.917 10 <sup>2</sup>	1.44 10 <sup>10</sup>	35.0	41.5
					35.1 ± 0.3	47.7 ± 0.4
6.72	0	0.937	5.909 10 <sup>4</sup>			
6.76	1.13 10 <sup>-5</sup>	0.855	2.355 10 <sup>4</sup>	2.31 10 <sup>8</sup>	34.7	41.7
6.73	2.27 10 <sup>-5</sup>	0.662	7.844 10 <sup>3</sup>	5.34 10 <sup>8</sup>	35.1	42.0
6.74	3.41 10 <sup>-5</sup>	0.690	8.888 10 <sup>3</sup>	2.12 10 <sup>8</sup>	34.8	41.8
6.78	4.55 10 <sup>-5</sup>	0.673	8.236 10 <sup>3</sup>	5.71 10 <sup>7</sup>	34.6	41.8
6.76	5.68 10 <sup>-5</sup>	0.555	4.982 10 <sup>3</sup>	3.50 10 <sup>8</sup>	34.9	41.9
6.74	6.53 10 <sup>-5</sup>	0.560	5.085 10 <sup>3</sup>	3.50 10 <sup>8</sup>	34.8	41.8
6.76	7.67 10 <sup>-5</sup>	0.504	4.067 10 <sup>3</sup>	3.22 10 <sup>8</sup>	34.8	41.8
6.72	8.53 10 <sup>-5</sup>	0.502	4.039 10 <sup>3</sup>	1.80 10 <sup>8</sup>	34.7	41.8
6.76	1.14 10 <sup>-4</sup>	0.364	2.289 10 <sup>3</sup>	2.51 10 <sup>8</sup>	34.9	41.9
6.74	1.71 10 <sup>-4</sup>	0.311	1.804 10 <sup>3</sup>	2.72 10 <sup>8</sup>	34.8	41.9
					34.8 ± 0.3	41.9 ± 0.2
					35.1 ± 0.7	41.6 ± 0.6

<sup>a</sup> log β ± t<sub>0.95</sub>σ, with t<sub>0.95</sub> = 2.262 for 10 values (9 degrees of freedom), and t<sub>0.95</sub> = 2.045 for 30 values (29 degrees of freedom).

**Table 4: Stability constants for humic complexes used in this study. The constants that take into account the reduction of M(VI) are calculated using the data from Table 2.**

Equilibrium	log $\beta_{n,m,z}$		
	Pu	Np	U
$M^{3+} + HA(III) \rightleftharpoons MHA(III)$	6.2		
$MO_2^{2+} + 3/2 H_2 + 4H^+ + HA(III) \rightleftharpoons MHA(III) + 2 H_2O + 3 H^+$	57.3	20.3	
$M^{3+} + OH^- + HA(II) \rightleftharpoons MOHHA(II)$	13		
$MO_2^{2+} + 3/2 H_2 + 3H^+ + HA(II) \rightleftharpoons MOHHA(II) + H_2O + 3 H^+$	50.3	13.3	
$M^{3+} + 2 OH^- + HA(I) \rightleftharpoons M(OH)_2HA(I)$	17.6		
$MO_2^{2+} + 3/2 H_2 + 2H^+ + HA(I) \rightleftharpoons M(OH)_2HA(I) + 3 H^+$	41.1		
$M^{3+} + CO_3^{2-} + HA(I) \rightleftharpoons MCO_3HA(I)$	12.4		
$MO_2^{2+} + 3/2 H_2 + 4H^+ + CO_3^{2-} + HA(I) \rightleftharpoons MCO_3HA(I) + 2 H_2O + 3 H^+$	63.5		
$M^{4+} + HA(IV) \rightleftharpoons MHA(IV)$	16.0	13.2	18.2
$MO_2^{2+} + H_2 + 4H^+ + HA(IV) \rightleftharpoons MHA(IV) + 2 H_2O + 2 H^+$	50.1	24.6	28.1
$M^{4+} + 4 OH^- + HA(I) \rightleftharpoons M(OH)_4HA(I)$	52.0	49.3	54.4
$MO_2^{2+} + H_2 + 2 H_2O + HA(I) \rightleftharpoons M(OH)_4HA(I) + 2 H^+$	30.9	5.5	9.0
$MO_2^+ + HA(I) \rightleftharpoons MO_2HA(I)$	4.6	4.6	
$MO_2^{2+} + 1/2 H_2 + HA(I) \rightleftharpoons MO_2HA(I) + H^+$	20.0		
$MO_2^{2+} + HA(II) \rightleftharpoons MO_2HA(II)$	6.2		6.2
$MO_2^{2+} + OH^- + HA(I) \rightleftharpoons MO_2OHHA(I)$	14.05		14.7

Following the recommendation in [71],  $H^+$  issued from the hydrogen oxidation are not taken into account in  $\Delta z^2$  and  $\Delta \epsilon$ , and are thus written in italic.