Influence of Addition Order and Contact Time on Thorium(IV) Retention by Hematite in the Presence of Humic Acids

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The influence of addition order and contact time in the system hematite (α-Fe₂O₃)–humic acid (HA)–thorium(IV) (Th(IV)) was studied in batch experiments. Th(IV) is considered here as a chemical analogue of other actinides (IV). The sorption isotherms were acquired varying pH in the range 2–10 and HA concentration in the range 1–100 mg/L. As already observed by numerous authors, Th(IV) retention was hindered when HA and hematite were equilibrated beforehand during 24 h. As it has been observed in a previous study, this effect was drastic when the ratio between humic and surface (iron oxide) sites exceeds a critical value. However, when HA was added after a 24-h equilibration of the hematite–Th(IV) system, Th(IV) was barely desorbed from the iron oxide surface. Furthermore, no drastic effect of the ratio between humic and surface sites could be evidenced, as the increase of HA concentration only results in a slight monotonic decrease in Th(IV) retention. Increasing contact time between components of the systems only indicated slight Th(IV) retention variation. This was interpreted as a consequence of slow kinetic controls of both the Th(IV)–HA complexation and HA–hematite sorption.

Introduction
Organic colloids can enhance the mobilization of metallic pollutants in soils and sediments (1–6). Sorption phenomena of natural organic matter (NOM) are of a great importance on this account. The general affinity of NOM and its humic fractions toward mineral surfaces not only induces modifications of physicochemical properties, as surface potential or colloidal stability (7,8), but also provokes modifications of the NOM itself (9–12).

Humic substances (HS) are the alkaline extractable fraction of NOM and are operationally defined from the extraction procedure: (i) humin is the insoluble fraction at whatever pH; (ii) humic acids (HA) are the insoluble fraction in acidic pH; (iii) fulvic acids (FA) are the soluble fraction whatever pH (sorbing on XAD resin) (13). HS can be now represented as aggregates of aromatic molecules (mostly phenolic) carrying a large number of carboxylic functions (14–16). The cohesion of these aggregates is through more or less weak bonding including van der Waals interactions or hydrogen bonding. Because of their high functionality, HS can strongly complex multivalent elements and modify their retention by minerals (17–21).

The association of thorium(IV) (Th(IV)) with HA is strong and has been observed on the field (22–25) and quantified (26–28). Th(IV) is often used as a chemical analogue for the other actinides (IV) (29). Solubility of actinides (IV) is fairly constant within the series, i.e., 10⁻⁴–10⁻³ M if pH ≥ 4 (30,31). Th(IV) seems to be preferentially associated with the highest relative molecular weight fraction of the NOM, and this association seems to be kinetically governed (32,33).

Humic acids are known to reduce redox-sensitive actinides, i.e., Pa, Np, and Pu (34–40) due to either the low redox potential of aqueous solution of HA (41–44) and/or by the preferential complexation of multicharged cations (45). The +IV oxidation state of the actinides seems to be stabilized by the humic complexation.

Thermodynamic description of the metallic cation retention by mineral surface in the presence of HA has often led to a deviation from additivity rules of interactions models (46–48) if the modeling is performed in a sufficiently wide parametric interval. Fractionation of HA induced by sorption on mineral surfaces should imply modification of HA aggregates and therefore modification of complexing properties of these aggregates. On the other hand, some authors have reported an influence of addition order. If the influence noted by Davis (19) was moderate in the case of Cu(II) on γ-alumina, it was clearly strong in the case of Zr–Hf(IV) on kaolinite (18). These authors compared the systems where (i) the mineral surface and HA were pre-equilibrated before any addition of metallic cation and (ii) the mineral surface and metallic cation were equilibrated beforehand and HA was added afterward. Liu and Gonzales (49) did not detect any noticeable difference when HA was pre-equilibrated or added simultaneously with divalent metals on montmorillonite, but the authors did not equilibrate the metal with the mineral surface beforehand.

For a predictive modeling of metal (IV) retention by mineral surface in the presence of HA, one has to understand the mechanism of these phenomena. Therefore, to illustrate the different cases we have studied the following pre-equilibrated systems: (i) hematite and HA equilibrated before any addition of Th(IV); (ii) hematite and Th(IV) equilibrated before any addition of HA; (iii) Th(IV) and HA pre-equilibrated before any addition of hematite.

Experimental Section
Materials. The colloidal hematite suspension and humic acids were the same as the one used in previous studies (17,50,51). Briefly, hematite was obtained from AEA Harwell and characterized by Cromières et al. (50, 51): diameter D = 55 nm; specific surface Sₚ = 19 m²/g; proton exchange capacity (PEC) = 3.8 × 10⁻³ eq/g. Purified Aldrich HA was characterized by Kim et al. (52): PEC = 5.4 × 10⁻³ eq/g.

The initial solution of thorium (²³³Th in 2 N HNO₃) was obtained from Amersham. This solution was diluted in order to obtain a 1.09 × 10⁻³ M stock solution in 0.9 M NaClO₄ and 0.2 M HNO₃. All other chemicals were reagent grade, and Millipore filtered water purged with Ar(g) was used (Milli-Q).

pH Measurement. The pH measurement was done using a TACUSSEL pH meter (PHM 220 MeterLab) with a combined TACUSSEL electrode (Radiometer type XC 161, modified NaClO₄, 0.1 M, NaCl 10⁻² M). Calibration in [H⁺] is performed...
with commercial buffers (Prolabo, pH = 4, 7, and 9). The pH of the stock solution of colloidal hematite is about 1, which minimizes the CO$_2$(g) dissolution. Nevertheless, the surface of solution was swept with Ar(g) to minimize the dissolution of CO$_2$(g) in the suspensions.

**Preparation of the Suspension.** The sorption experiments were conducted at room temperature according to a batch procedure in 10-mL polycarbonate vials sealed with screwcaps (Nalgene).

Different modus operandi were used depending on the order of addition of the constituents. In all the experiments, the hematite suspension was always prepared first.

**Hematite Suspension.** As the colloidal hematite suspension was stored under acidic conditions (pH = 1), the colloidal phase was rinsed with Milli-Q water in order to eliminate excess acid and to eliminate the last traces of chloride ions. An aliquot of the initial solution (1.5 g L$^{-1}$) was dispersed into Milli-Q water (9.5 mL) in centrifuge tubes and ultrasonically (Bioblock 35 kHz) shaken for 30 min. The obtained suspension was then ultracentrifuged at 50,000 rpm for 30 min, and 6 mL of the supernatant were discarded; this operation is repeated 3 times. The concentration of the hematite suspension was fixed at the desired concentration by diluting the rinsed solution by the background electrolyte (NaClO$_4$). The pH was adjusted to the desired value. The obtained suspension was shaken for 24 h to allow equilibration of the suspension.

Under the same conditions, inorganic carbon concentration has been estimated to be less than 5 $\times$ 10$^{-3}$ M (53,54), which induces only a weak influence on Th(IV) speciation (28,55).

Depending on the order of addition, either HA or Th(IV) was added to the suspension.

**HA Addition.** When the hematite suspension was equilibrated, aliquots of the HA stock solution were added. The pH value was adjusted using freshly prepared 0.1 M HClO$_4$ or NaOH and shaken for the appropriate time.

**Th(IV) Addition.** When the suspension was equilibrated, an aliquot of the Th(IV) stock solution was added to obtain a final concentration of 1.15 $\times$ 10$^{-12}$ M; the pH was adjusted at the desired value. The solution was shaken again for the appropriate time.

**Separation of the Colloidal Suspension.** As in previous studies (17,28), we used the separation methods used by Cromières et al. (50) to minimize the Th(IV) adsorption onto the vessel walls (54,56). The retention was calculated referring to the activity measured in the suspension and not referring to the total activity introduced in the ultracentrifuge tube.

After the appropriate equilibrium time, three 0.5-mL aliquots of the suspension were sampled for thorium activity measurement ($A_s$) is the mean of the measurements). The colloids were separated from the liquid phase by ultracentrifugation (90 min, 50,000 rpm), the pH of the supernatant was measured, and three other aliquots of 0.5 mL were sampled from the supernatant for thorium activity measurement ($A_d$). The activities of $^{228}$Th were measured by liquid scintillation counting. The sample aliquots were added to 4 mL of liquid scintillator (Ultima Gold AB). The activity measurements were performed after one month in order to attain the secular equilibrium of $^{228}$Th with its daughters.

**Sorption Parameters.** The sorption percentage $R$ was calculated from the activities of the suspension ($A_s$) and of the supernatant ($A_d$) according to the following equation

$$R (\%) = \left( 1 - \frac{A_d}{A_s} \right) \times 100$$  \hspace{1cm} (1)

For the sake of comparison with independent results, the results are presented vs the ratio of available binding site [HA]/[SOH] defined as

$$\frac{[\text{HA}]}{[\text{SOH}]} = \frac{(C_{\text{HA}} \text{ (g/L)})(5.4 \times 10^{-3} \text{ (eq/g)})}{(C_{\text{a-Fe$_2$O$_3$}} \text{ (g/L)})(3.8 \times 10^{-5} \text{ (eq/g)})}$$  \hspace{1cm} (2)

where [HA] is the concentration of humic sites and [SOH] is the concentration of surface sites.

**Results and Discussion**

**Pre-Equilibration of Hematite and HA.** In Figure 1 are reported pH isotherms obtained in Reiller et al. (17) for the systems where hematite (50 mg/L) and HA (0 and 10 mg/L) are pre-equilibrated for 24 h (diamond symbols) before any addition of Th(IV) at 0.1 and 10$^{-3}$ mol NaClO$_4$/L. New data obtained for $\alpha$-Fe$_2$O$_3$ = 500 mg/L at 0.1 mol NaClO$_4$/L are also reported (grey circles). Plotting these results in $K_d$ (mL/g) = [Th$^{\text{tot}}$/Th$^{\text{res}}$] (data not shown) show no differences with the results obtained in (17). Hence, the sorption of Th(IV) on hematite can be directly compared in the two systems.

The results of HA retention in the systems were reported earlier (17).

The decrease in metal retention when HA is pre-equilibrated with the solid is a classical observation (18–21,57). Takahashi et al. (18) postulated that this phenomenon was due to the weak interaction of tetravalent cations, i.e., Zr(IV) and Hf(IV), with humic substances. The known interaction of Th(IV) with NOM observed in aquatic, marine, and groundwater systems seems to contradict the latter hypothesis (22–24). Moreover, strong interaction constants were determined for Th(IV) and Np(IV) with humic acid in pH ranges relevant to natural waters (28,58,59). Thus, the strength of the interactions between HA and metal ions does not seem to be the main factor implied. Under our conditions, humic sites are mainly present in solution, and their concentration in solution increases with pH as ionization increases. When Th(IV) is added in the system, competition occurs between free humic sites and hematite surface sites. This competition is strongly in favor of HA in the acidic–neutral pH range, high strength of complexation between Th(IV) and HA, whereas for pH > 8, complexation by surface sites increases up to 50%. Hence in this system, where hematite is pre-equilibrated with HA, organic matter controls Th(IV) behavior.

Decreasing the ionic strength to 10$^{-3}$ M (open diamonds in Figure 1) does not seem to have any effect in this system. Similarly, ionic strength had a very weak or no influence on HA retention onto this substrate as evidenced in the previous study (17). As a matter of fact, the actual colloidal state of this $\alpha$-Fe$_2$O$_3$ sample limits the effect of ionic strength (50,60).

Up to now the tentative modeling of ternary systems, i.e., solid–humic–metal, revealed that the additivity rule cannot be simply applied (46–48). As a matter of fact, a large number of authors has clearly shown that slow sorption kinetic, fractionation phenomena, and solid-phase dissolution were implied (9,12,61–66). Thus, a reliable thermodynamic modeling of these systems is difficult to assess without prior assessment of an actual equilibrium state.

**Pre-Equilibration of Hematite and Th(IV).** The results obtained when Th(IV) is pre-equilibrated with hematite before any addition of HA (square symbols in Figure 1) do not show the same effect as when the humic acid is pre-equilibrated. In this case, the effect of HA on Th(IV) retention is weaker than in the former case. This weaker influence of HA when added after hematite–metal equilibration was reported by only few authors (18,19). The effect was not that spectacular in the case of Cu(II) on γ-alumina (19) but seems equivalent in the case of Zr(IV)/Hf(IV) on kaolinite (18). This effect was not detected in the case of silica by Takahashi et al. (18).

The influence of HA concentration on Th(IV) retention by colloidal hematite at different pH values reported by Reiller et al. (17) is reported in Figure 2 using closed symbols. The
equilibration time was 24 h for hematite–HA suspension and 24 h after the addition of Th(IV). Comparable batch experiments were performed by equilibrating Th(IV) with hematite for 24 h prior to addition of HA in the suspension. The final suspension was then shaken for another 24 h. The results are plotted using open symbol in Figure 2.

It was noted in Reiller et al. (17) that the organic layer at the hematite surface has a marked influence on the Th(IV) sorption when the ratio \[\frac{[\text{HA}]}{[\text{SOH}]}\] was about 3. Such an effect could not be evidenced when Th(IV) is equilibrated with hematite before any HA addition. Even when \[\frac{[\text{HA}]}{[\text{SOH}]} \approx 30\], \(R(\text{Th})\) is only decreased from 99.6 to 93% at \(pH \approx 6.5\). Th(IV) retention in these systems still seems to increase with pH in this interval, as it was in Reiller et al. (17), even if the \(R(\text{Th})\) values could not be discriminated statistically.

In the study of Takahashi et al. (18) for the HA–kaolinite system, the ratio \([\text{HA}]/[\text{SOH}]\) can be calculated as

\[
\frac{[\text{HA}]}{[\text{SOH}]} = \frac{(30 \times 10^{-3} \text{ (g/L)}) (6.1 \times 10^{-3} \text{ (meq/g)})}{(2 \text{ (g/L)}) (2.9 \times 10^{-3} \text{ (eq/g)})} = 3.2
\]

This value is lower than the one used in this study \([\text{HA}]/[\text{SOH}] \approx 30\). In the case of our hematite sample, no difference in the addition order could be anticipated at a ratio of 3.2 from the results in Figure 2. Nevertheless, one
should keep in mind that kaolinite is less efficient in retaining HA than hematite (18).

The results obtained are not easily interpreted. Nevertheless, given the preferential complexation of Th(IV) by the highest molecular mass fraction of NOM (32,33) and the kinetic control of the NOM sorption by mineral surface (12,61,66), a tentative explanation of this comportment can be proposed. van de Weerd et al. (61) modeled the results of Gu et al. (12) and proposed different sorption kinetics for six fractions representing NOM, namely, hydrophobic and hydrophilic fractions of size <3 kDa, 3–100 kDa, and >100 kDa. The lower mass fraction and the more hydrophobic fraction have faster kinetics. Through this modeling, the higher mass fractions reach sorption equilibrium in times ranging from 100 hours to more than 900 h. These modeling results were experimentally confirmed by Hur and Schlautman (66) in the case of purified Aldrich humic acid.

Interestingly, the hematite sample used by Gu et al. (12) and the one used in Reiller et al. (17) and in this study too have very similar properties except for the size of the particles, i.e., D = 150–300 nm, Ssp = 10 m²/g, anion exchange capacity = 3.86 × 10⁻⁵ mol/g. Nevertheless, the experiments of Gu et al. (12) were performed at pH = 4.1. The comparison of our results with Gu et al. (12) experiments and with van de Weerd et al. (61) modeling results can only be qualitative. The experiments by Hur and Schlautman (66) could be compared to our results apart from the lack of site density determination and the difference in specific surface area (7.41 m²/g).

In our case, no fraction greater than 100 kDa can be anticipated with HA. But depending on the concentration, the fraction 3–100 kDa could reach sorption equilibrium after 500 h for hydrophobic fractions and more than 900 h for hydrophilic fractions (61). Given the short time of our experiments (24 h), the sorption of these fractions could not have reached equilibrium. This is further confirmed by the observation of Hur and Schlautman (66). Therefore, when HA is pre-equilibrated with hematite over 24 h, the higher mass fractions are not in equilibrium with the hematite surface and are thus present in “solution”. When Th(IV) is added to this suspension, the complexation with higher mass fractions would lead to its presence in the supernatant.

Moreover, the formation of inner-sphere surface complexes of Th(IV) on this hematite sample, evidenced by Cromieres et al. (50), could help to explain this unexpected behavior.

When Th(IV) is pre-equilibrated with hematite, the complexation between the higher mass fraction in solution and sorbed Th(IV) seems less probable in the time frame of the experiment, and the metal retention by hematite would be more important.

Gu et al. (12) used a 1% hematite stock solution, diluted to 1/5 (i.e., ≈ 2 g/L or [=SOH] = 7.7 × 10⁻⁵ eq/L), and the high concentration postulated by van de Weerd et al. (61) was 14.4 mg of carbon/L (12 meq/g of carbon or [=HA] = 1.7 × 10⁻⁴ eq/L). This leads to a ratio [=HA]/[=SOH] = 2.24. This value is very close to the retention drop evidenced in Reiller et al. (17). The experiments reported in Figure 2, [=HA]/[=SOH] ≥ 5, were thus performed in conditions where higher mass and hydrophobic fractions would not be in equilibrium with the hematite surface.

The question of Th(IV) sorption reversibility on the hematite sample must also be addressed. Ho and Doern (67) showed that uranium(VI) (U(VI)) was partly irreversibly bound onto hematite at pH = 6.2, where highly hydrolyzed (UO₂)₃(OH)₅⁺ was the major species under these conditions (31,68). The total reversibility could only be obtained lowering pH to 4 within 24 h, where UO₂²⁺ is the major species. Under our conditions, we can estimate, referring to Neck and Kim (30), that Th(OH)₁⁺ and Th(OH)₄(aq) are the major Th(IV) species in solution in the interval 6 ≤ pH ≤ 9. As in the case of U(VI), the presence of strongly hydrolyzed Th(IV) species can be responsible of the irreversible process. However, studies on sorption reversibility of thorium (IV) are scarce, and this phenomenon is difficult to take into account without a proper analysis.

**Influence of Contact Time**. The influence of slow kinetics in HA chemistry has been evidenced either in the case of metal complexation (33,69), retention by mineral surface (12,66), or even in the case of structural rearrangement (70,71). Hence, contact time between HA and pre-equilibrated hematite–Th(IV) systems at pH ≈ 7 was increased from 24 h to 1, 2, and 3 weeks (168, 336, and 504 h). Results are reported in Figure 3 compared to the results of Reiller et al.

**FIGURE 3. Influence of the addition order of the components, of the contact time, and of HA concentration on the retention of Th(IV) at pH ≈ 7.**

<table>
<thead>
<tr>
<th>[mHA]/[mSOH]</th>
<th>R(Th) (%)</th>
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<tr>
<td>0.5</td>
<td>100</td>
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<tr>
<td>0.1</td>
<td>90</td>
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<tr>
<td>0.05</td>
<td>80</td>
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![Graph showing the influence of the addition order of the components, of the contact time, and of HA concentration on the retention of Th(IV) at pH ≈ 7.](image)
(17) (α-Fe$_2$O$_3$–HA, 24 h; α-Fe$_2$O$_3$–Th(IV), 24 h; pH = 7.16, closed squares) and to the results presented in Figure 2 (α-Fe$_2$O$_3$–Th(IV), 24 h α-Fe$_2$O$_3$–HA, 24 h; pH = 7.26, open squares) obtained at about the same pH value. A slight decrease in the $R$(Th) value could be evidenced in Figure 3 when contact time is increased. The differences between the different contact times are only statistically significant when $[\text{HA}]/[\text{SOH}]$ increases. Nevertheless, the retention drop is undoubtedly less significant comparing to the Th(IV) sorption hindrance provoked by the formation of the organic layer as noted earlier (cf. Figure 2). These results indicate that the slow sorption, or complexation, kinetics has only a minor effect in the time frame of these experiments. It can be suggested that a longer equilibration time could induce a more intense desorption of Th(IV) from hematite surface.

Quigley et al. (72) and Guo et al. (73) showed that the complexation of Th(IV) is more intense for the hydrophilic fraction of marine organic matter, especially in the case of acid polysaccharides (size $\leq 0.5\mu m$). In the model developed by van de Weerd et al. (61), the hydrophilic fractions have the slowest sorption kinetics. If Th(IV) is preferentially complexed by higher sized and hydrophilic fractions, then the exchange between hematite surface and organics in solution seems not to be favored, and Th(IV) should be preferentially fixed on the solid in the time frame of the experiment.

Interestingly, studying the leaching of borosilicate glasses, Dran et al. (74) showed that Zr(IV) was highly retained in the
altered layer but also leached from borosilicate glasses by solutions containing Aldrich humic acids as the concentration of Zr(IV) increased from 2.2 × 10⁻³ M and 0.02 mg Zr/L with no HA up to 1.1 × 10⁻² and 0.1 mg Zr/L with 80 mg HA/L. The authors also showed that the kinetics must be very slow at 90 °C during 168 h.

Pre-Equilibration of HA and Th(IV) and Influence of Contact Time. For these experiments, hematite concentration was lowered to 50 mg/L. The [HA]/[SOH] ratio was the same as in Figures 2 and 3, so the HA concentrations were lowered to a tenth of those used in Reiller et al. (17) (Figure 4, closed squares). A similar retention pattern is obtained (Figure 4, gray squares). Nevertheless, it can be observed that the retention of Th(IV) is slightly higher in this series than in the one previously obtained. These differences cannot be interpreted, and further work is in progress to understand this behavior.

The modeling of the interaction between metallic cations and HA has recently been presented as kinetically controlled (69). This kinetic control seems to lead to an irreversible part of the complexation. This seems to be in agreement with the complexation of Th(IV) in marine systems (33).

The influence of contact time between HA and Th(IV) on the retention by α-Fe₂O₃ at pH = 7, as well as the results obtained in Reiller et al. (17) for the same conditions, are reported in Figure 4a. As in the preceding cases, the contact time in the time frame of the experiments has only a weak influence on the final result. Nevertheless, a slight increase of Th(IV) retention by the solid phase can be noticed. This effect is barely statistically significant.

In these experiments, the contact times between HA and hematite are the same, i.e., 24 h. Consequently, these results only reflect the Th(IV) complexation by HA, assuming no effect on HA properties. Von Wandruszka et al. (71) evidenced an enhancement of the pyrene fluorescence in Th(IV)–HA systems when [Th(IV)] > 10⁻² M, indicating further aggregation of HA sample, but no pH indication is available in the original paper, the influence of ThO₂ solubility cannot be checked. Nevertheless, no such effect could be anticipated under our conditions where [Th(IV)] ≈ 10⁻¹² M.

The influence of contact time between Th(IV)–HA complex and the hematite surface is reported in Figure 4b. In these series of experiments, the Th(IV)–HA complex is equilibrated during about 1 month (29 and 34 days) before any contact with hematite. The contact time of the pre-equilibrated Th(IV)–HA complex with hematite was increasing to 9 and 28 days (open symbols). The results obtained in Reiller et al. (17) (black squares), and the ones that were reported in Figure 4a (hematite–HA 24 h/Th(IV) 24 h, gray squares; Th(IV)–HA 37 days/hematite 24 h, gray circles) are reported for the sake of comparison.

As in Figure 4a, a slight increase in Th(IV) retention can be observed when increasing contact time of the humic complex with hematite. Nevertheless, as in Figure 4a, this increase is barely statistically significant. A tentative explanation could be linked to the discussion of preferential complexation of Th(IV) by higher mass fraction and to the kinetics control of Th(IV)–HA complex. On one hand, it has been proposed that Th(IV) is preferentially complexed by the higher-sized and hydrophilic fractions of NOM (72). On the other hand, from the works of van de Weerd et al. (61), these fractions have the slowest sorption kinetic that would imply not only a slow desorption of Th(IV) from hematite surface but also a slow sorption of pre-equilibrated Th(IV)–HA complex on the same hematite surface. A final step would be increasing contact times to larger values in order to test this hypothesis. Further works are in progress to test the validity of this hypothesis.

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