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1 **Montmorillonite colloids: II. Colloidal Size Dependency on Radionuclide**

2 **Adsorption**

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10

11 **Keywords**

12 Montmorillonite colloids, particle size effect, adsorption, radionuclides, nuclear waste
13 disposal

14

15 **Abstract**

16 Bentonite is a strong radionuclide (RN) adsorbent. As a consequence, it is proposed as one of
17 the engineered safety barriers in many concepts of nuclear waste disposal in granite
18 formations. Nevertheless, in contact with groundwater of low ionic strength, montmorillonite
19 colloids may be released from the bentonite buffer and transported towards the biosphere.
20 During the transport of colloids in bedrock fractures, size separation of clay colloids may
21 occur, that may potentially also affect the RN mobility. In this work, the RN adsorption
22 (Th(IV), U(VI), Np(V), Tc(VII) and Pu(IV)) onto size fractionated montmorillonite colloids
23 was studied in a synthetic, carbonated groundwater. We combined batch adsorption
24 experiments and geochemical modelling. U(VI), Np(V) and Tc(VII) did not adsorb to the
25 montmorillonite colloids in the synthetic groundwater. Adsorption of Th(IV) and Pu(IV) was
26 strong but, within experimental uncertainties, not significantly affected by the mean colloidal
27 size. In this case, average K_D values could in principle be used in reactive transport modelling.
28 Montmorillonite clay colloids obtained by fractionation of the raw clay material but in the
29 presence of organic matter during the initial separation step exhibited significantly reduced
30 affinity for Th and Pu.

31

32 **1 Introduction**

33 The deep geological repository concept for high-level nuclear waste includes several barriers
34 (technical, geotechnical and geological) to isolate or retard the potential transport of
35 radionuclides (RNs) towards the biosphere. Compacted bentonite is planned to be the
36 geotechnical barrier surrounding the metal canisters (SKB, 2010). Bentonite consists mainly
37 of montmorillonite (smectite clay) and is chosen for its favourable swelling capacities, its
38 high cation adsorption capacities and its strong mechanical stability (Karnland et al., 2006). In
39 case of canister failure, this geotechnical barrier will retard the RN transport towards the
40 biosphere. However, in contact with groundwater of low ionic strength, the bentonite barrier
41 may release stable montmorillonite colloids (Geckeis et al., 2004; Missana et al., 2003;
42 Schäfer et al., 2012). The montmorillonite colloids can be transported through the geosphere
43 via advective water flows (Möri et al., 2003). To be able to estimate the colloid facilitated
44 transport of RNs, a large and complex set of parameters has to be considered.

45 Colloidal transport of montmorillonite through bedrock fractures depends on the ground water
46 flow velocity (Zhang et al., 2012). At high water flow velocity, i.e. in clean bedrock fractures
47 with a low amount of fracture filling material (FFM), a laminar water flow is expected which
48 can separate the colloids according to their mass (for the same specific density), and thus their
49 size. In the opposite, if the fracture contains sufficient amount of FFM, the FFM may be
50 simplified seen as a porous medium, where larger colloids can be transported in the fastest
51 streamlines due to size exclusion effects (Bradford et al., 2002; Sirivithayapakorn and Keller,
52 2003). Since size separation of montmorillonite colloids may occur in bedrock fractures, their
53 size, morphology, stability and RN adsorption capacities are some of the important
54 parameters for estimating colloid facilitated transport of RNs. These parameters should
55 therefore be included in reactive transport modelling. In a recent study on montmorillonite
56 colloidal stability performed at various ionic strengths (Norrfors et al., 2015), no dependency
57 on the montmorillonite size could be observed. Based on this study, hydrodynamic induced
58 size fractionation and the potential formation of different colloid size fractions will not
59 influence their stability under the same geochemical conditions but some colloids may be able
60 to migrate further due to e.g. steric stabilisation effects by natural occurring dissolved organic
61 matter as fulvic acid (FA).

62 It is of high importance to examine how the RN adsorption depends on the clay colloid size
63 and thus, the total exposed surface area. Previous studies have demonstrated a size-dependent
64 reactivity of hematite nano-mineral surfaces on Cu^{2+} adsorption (Madden et al., 2006). If the
65 RN adsorption is shown to depend on the montmorillonite colloidal size, owing to their
66 exposed lateral surface area, the amount of RNs transported through the bedrock would be
67 over- or underestimated in the reactive transport models used today (Vahlund and
68 Hermansson, 2006). Alternatively, if the exposed surface area does not have a large impact on
69 the adsorption capacities, averaged adsorption capacities for montmorillonite can be used, as
70 in the case of cation exchange, which is thought to be independent of colloidal size (Stul and
71 Van Leemput, 1982). Tournassat et al. (Tournassat et al., 2003) suggested a model where the
72 amount of edge sites can be calculated from the aspect ratio and the density of the clay
73 particles by assuming a site density of silanol and aluminol edge sites per mass clay. Given
74 the same density of all clay particles, the amount of edge sites are proportional to the aspect
75 ratio. This model was further developed by the authors in a previous work (Norrfors et al.,
76 2015) where montmorillonite colloids were successfully separated into fractions with varying
77 mean colloid sizes. These colloids were used in the adsorption study presented in this work.

78 Accordingly, this work aims to investigate the influence of the exposed lateral surface area of
79 montmorillonite colloids (which is related to their size) on the adsorption of trace
80 concentrations of RNs in a synthetic groundwater (SGW) representing a glacial meltwater
81 type (Geckeis et al., 2004; Kunze et al., 2008; Möri et al., 2003). In this work, the term clay
82 colloids refer to aggregates, consisting of stacks of several clay mineral layers. Seven
83 montmorillonite dispersions with different mean particle sizes, including one containing
84 fulvic acids (FA), were used for adsorption studies with $^{232}\text{Th}(\text{IV})$, $^{99}\text{Tc}(\text{VII})$, $^{233}\text{U}(\text{VI})$,
85 $^{237}\text{Np}(\text{V})$ and $^{242}\text{Pu}(\text{IV})$ during a long (up to six months) equilibration time. The 2 sites
86 protolysis non-electrostatic surface complexation and cation exchange (2 SPNE SC/CE)
87 model (Bradbury and Baeyens, 2011) was used to predict the uptake of RNs. In addition, we
88 attempted to estimate the influence of expected amounts of edge sites, calculated for each
89 particle size, on the RN adsorption process.

90

91 **2 Material and Methods**

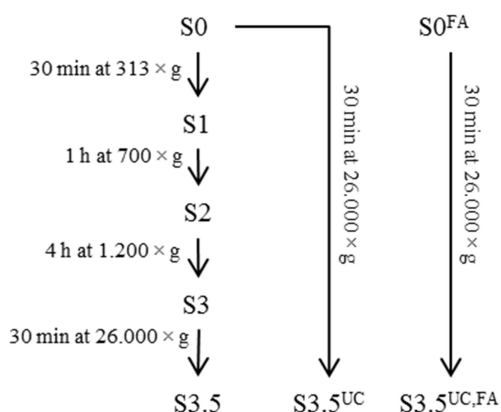
92 **2.1 Montmorillonite colloids and fulvic acids**

93 Various dispersions containing size fractionated montmorillonite colloids originating from
94 raw Wyoming MX80 bentonite ($M_w = 372.6 \text{ g/mol}$ (Karlund et al., 2006)), American Colloid
95 Co., were used in this study. Preparation and characterization of the montmorillonite
96 dispersions are explained in detail in previous work (Norrfors et al., 2015). A summary of the
97 preparation protocol is presented schematically in Figure 1. Details of centrifugation speeds
98 and times are given in Table 1. In brief, the un-purified MX80 bentonite (10 g/L) was placed
99 into carbonated synthetic groundwater (SGW) and settled during three days. The supernatant
100 was collected and named dispersion S0. The dispersion S0 was further separated into different
101 size fractions by sequential or direct centrifugation. In the sequential (ultra-)centrifugation, S0
102 was first centrifuged to obtain supernatant S1. Thereafter, S1 was centrifuged to obtain
103 supernatant S2 etc., resulting as well in supernatants S3 and S3.5. For comparison, S0 was
104 also directly ultra-centrifuged (UC) to obtain the dispersion S3.5^{UC}. It was found that the
105 dispersions S3.5 and S3.5^{UC} exhibit the same size distribution of colloids despite the different
106 separation protocol. All dispersions have been characterized according their size, chemical
107 composition, mineralogical composition and colloidal concentration in a previous paper,
108 where all details can be found (Norrfors et al., 2015). Suspension concentration was adjusted
109 to 20 mg/L in the RN batch adsorption experiments.

110 To be able to estimate the exposed lateral surface and thus the amount of adsorption edge sites
111 in each montmorillonite dispersions, the clay particles were assumed to be disc-shaped
112 (Norrfors et al., 2015). Then, their mean disc diameter and height were calculated by
113 equations developed by Jennings and Parslow (Jennings, 1993; Jennings and Parslow, 1988).
114 For this purpose, the mean colloidal sizes of each dispersion measured by different techniques
115 were used in the equations to obtain the mean disc sizes and heights, see Table 1 and
116 (Norrfors et al., 2015). These diameters are mean values for the whole size distribution of
117 colloids in the respective dispersions. S0 includes both larger and smaller sized colloids,
118 whereas S3.5 and S3.5^{UC} only include smaller colloids and were therefore less polydisperse.

119 The amount of adsorption edge sites was calculated according to the work of White and
120 Zelazny (White and Zelazny, 1988) and Tournassat et al. (Tournassat et al., 2003), assuming a
121 clay density of 2.7 g/cm^3 . The calculated mean clay particle disc diameters were used to
122 determine their lateral area from which the amount of sites in the clay dispersions could be
123 estimated (in mmol/kg). The estimated amounts of sites are presented in Table 1.

124 Complementary, one clay suspension was prepared in presence of FA, representing natural
 125 organic matter. The fulvic acid (FA-573) has been extracted from a natural groundwater
 126 (Gohy573) of the Gorleben site, Germany (Wolf et al., 2004). A small amount of FA was
 127 weighed, dissolved in NaOH and diluted in a separate clay dispersion (10 g raw MX80
 128 bentonite in 1 L SGW). Thereafter, this FA-clay dispersion was ultra-centrifuged during the
 129 same time and at the same speed as the dispersion $S3.5^{UC}$, and denoted $S3.5^{UC,FA}$. The final
 130 concentration of FA in the batch adsorption experiment was approximately 1.9 mg/L after
 131 dilution of the dispersion $S3.5^{UC,FA}$ to a concentration of 20 mg/L montmorillonite colloids.



132
 133 **Figure 1: Schematic diagram of bentonite fractionation into various aggregate size fractions by sequential**
 134 **and direct (ultra-)centrifugation.**

135
 136
 137 **Table 1: Dispersions used in the batch adsorption experiments, separation protocol performed, mean**
 138 **diameter of the clay discs and amounts of adsorption sites determined (Norrfors et al., 2015).**

Colloidal dispersion	Conditions of separation (C: centrifugation; UC: ultracentrifugation)	Mean diameter of clay discs (nm)	Amount of adsorption sites (mmol/kg)
S0	3 days sedimentation	1496	11.2
S1	C: 30 min (S0) at $313 \times g$	940	17.8
S2	C: 1 h (S1) at $700 \times g$	500	33.5

S3	C: 4 h (S2) at $1.200 \times g$	250	67.0
S3.5	UC: 30 min (S3) at $26.000 \times g$	258	64.7
S3.5^{UC}	UC: 30 min (S0) at $26.000 \times g^a$	246	67.9
S3.5^{UC,FA}	UC: 30 min (S0) at $26.000 \times g^a$	187	89.5*

139 ^a: one step ultra-centrifugation from colloidal dispersion S0 obtained after stirring and sedimentation of a
140 MX80 dispersion at 10 g/L in presence or absence of 11.8 mg/L FA . *: Amount of sites estimated from the
141 mean colloidal size, i.e. neglecting potential site occupancy by FA.

142

143 2.2 Synthetic Groundwater (SGW)

144 Synthetic, carbonated groundwater (SGW) is used as background electrolyte to simulate a
145 glacial meltwater of low ionic strength, similar to the granitic groundwater present at the
146 Grimsel Test Site (Geckeis et al., 2004; Kunze et al., 2008; Möri et al., 2003). The SGW is
147 prepared by mixing different salts (NaCl, CaCl₂, MgCl₂, NaF, Na₂SO₄ and NaHCO₃), yielding
148 the composition presented in Table 2. The total ionic strength is 1.6 mM and the pH is $8.4 \pm$
149 0.1 prior to contact with montmorillonite colloids and radionuclide cocktail.

150

151 **Table 2: The chemical composition of the synthetic groundwater (SGW) used as background electrolyte in**
152 **all samples (Norrfors et al., 2015).**

Element	Concentration (mM)
Na ⁺	1.2
Ca ²⁺	0.05
F ⁻	0.1
Cl ⁻	0.074
SO ₄ ²⁻	0.04
HCO ₃ ⁻	1.0
pH	8.4 ± 0.1

Eh _(SHE)	+0.35 ± 0.05 V
---------------------	----------------

153

154 **2.3 Radionuclide cocktail**

155 A radionuclide cocktail containing the elements: ²³²Th, ⁹⁹Tc, ²³³U, ²³⁷Np and ²⁴²Pu was
156 prepared in a glove box under Ar atmosphere in 0.1 M HCl. The cocktail was used to spike
157 the seven clay dispersions, diluted to 20 mg colloids/L in the SGW. The initial (total) RN
158 concentrations in all adsorption samples was checked by analysing the top 0.5 mL out of a
159 total sample volume of 50 mL by ICP-MS. This yielded [²³²Th(IV)] = 10⁻⁸ M, [⁹⁹Tc(VII)] =
160 5·10⁻⁹ M, [²³³U(VI)] = 10⁻⁸ M, [²³⁷Np(V)] = 10⁻⁸ M and [²⁴²Pu(IV)] = 2·10⁻⁹ M. ²⁴²Pu was
161 added as ²⁴²Pu(III) to the radionuclide cocktail, but based on thermodynamic considerations,
162 Pu(III) was expected to oxidize to Pu(IV) due to pH adjustments under the SGW experimental
163 conditions utilized, as will be further discussed in section 3.1.6. All RNs concentrations
164 (except for Pu) were below the relative solubility limits in the carbonated SGW, according to
165 literature (Np(V) (Guillaumont and Mompean, 2003; Neck et al., 1992; Runde et al., 2002),
166 Tc(VII) (Alliot et al., 2009), U(VI) and Pu(IV) (Huber et al., 2011), Th(IV) (Östhols et al.,
167 1994)).

168

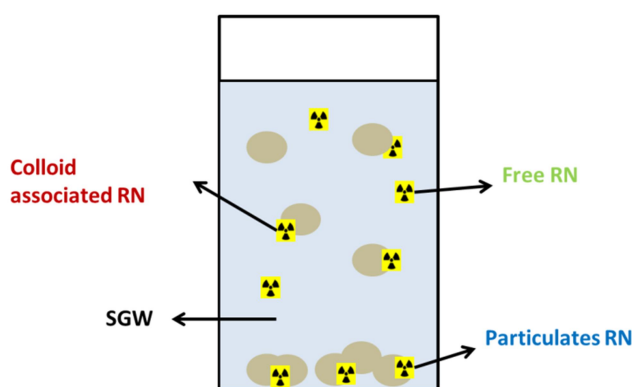
169 **2.4 Experimental conditions and procedure**

170 All experiments were performed at room temperature in a glove box under Ar atmosphere (<1
171 ppm O₂). pH was measured with a semi micro Ross electrode (81-03, Orion Co.) in
172 combination with a digital pH-meter (720A, Orion Co.). This set-up was calibrated using four
173 commercial buffer solutions (Merck). The redox potentials in the clay dispersions were
174 measured using an Orion 525A (Eh meter) and a Pt electrode combined with Ag/AgCl
175 reference system (Metrohm). Raw data were converted into Eh vs. standard hydrogen
176 electrode (SHE) by correcting for the potential of the reference electrode. A commercial
177 redox-buffer (+220 mV, Schott instruments) was used for calibration. An equilibration time of
178 30 min was applied for all Eh measurements. Uncertainties in Eh measurements were ± 50
179 mV (Altmaier et al., 2010; Kirsch et al., 2011).

180 Each batch adsorption sample was prepared in duplicate and contained 20 mg/L
181 montmorillonite in a total volume of 50 mL. For monitoring radionuclide adsorption, aliquots

182 of the samples were taken after 72 h (~3 days), 260 h (~2 weeks), 580 h (~1 month) and 3800
183 h (~6 months). Initially, the top 0.5 mL of the sample was analysed by ICP-MS to obtain the
184 amount of stable montmorillonite colloids in the dispersion. Thereafter, approximately 4 mL
185 of each sample was transferred into ultra-centrifugation vials, sealed by welding inside the
186 glove box and afterwards ultra-centrifuged (Beckman XL-90, rotor type 90Ti) for 1h at
187 90.000 rpm (centrifugal force of approximately $7 \cdot 10^5 \times g$). Subsequently, a volume of 0.5 mL
188 of the ultra-centrifuged supernatants was sampled and analysed by ICP-MS. This ultra-
189 centrifugation procedure has been proven to effectively remove montmorillonite colloids and
190 thereby the RNs associated to colloids (Altmaier et al., 2004). When the experiment ended
191 (i.e. after 6 months), all samples were characterised by $\text{pH} = 8.9 \pm 0.3$ and $\text{Eh}_{(\text{SHE})} = +230 \pm$
192 50 mV.

193 From the ICP-MS data, the distribution of RNs was calculated and defined as (i) the amount
194 of soluble species RNs in dispersion (%Free), (ii) RNs associated to montmorillonite colloids
195 (%Colloid) and (iii) the amount of RNs associated to particulates (i.e. settled particles,
196 %Part). This is illustrated in Figure 2. When present initially, 70% of the FA was found free
197 in the dispersion after fractionation. No distinction between soluble RNs species and
198 dissolved FA-RN complexes could be made with this method. The concentration of RNs as
199 soluble species was measured in the supernatant after ultra-centrifugation. Colloidal RN
200 concentration was determined from the difference in concentration before and after ultra-
201 centrifugation. Particulate RNs was the remaining RN concentration based on the initial
202 concentration. All results presented are mean values of duplicate samples with its standard
203 deviation. The dispersion S3.5 was proved to have the same size distribution as S3.5^{UC}.
204 Identical adsorption results were obtained for these two dispersions, indicating a good
205 reproducibility of the fractionation procedure developed (Norrfors et al., 2015).



206

207 **Figure 2: Schematic diagram of the radionuclide (RN) distribution in the batch adsorption samples, as**
208 **determined from ICP-MS measurements.**

209

210 K_D values for each RN were calculated for the overall RN adsorption as “average K_D values“,
211 which does not distinguish between suspended (%Colloids) and particulate (settled particles,
212 %Part) clay. The expression for K_D is given in equation 1:

$$213 \quad K_D = \frac{[RN]_{Tot} - [RN]_{free}}{[RN]_{free}} \cdot \frac{1}{m_{clay}} \quad (dm^3/kg) \quad (1)$$

214 where $[RN]_{Tot}$ and m_{clay} are the total, initial concentrations of RNs and montmorillonite,
215 respectively. $[RN]_{free}$ is the concentration of soluble species of RNs in solution after a given
216 equilibration time. A standard deviation of $\log(K_D \text{ (dm}^3\text{/kg)}) = 0.5$ was applied to all K_D
217 values, as suggested by Bradbury and Baeyens (Bradbury and Baeyens, 2011), due to
218 experimental uncertainties for strongly adsorbing elements.

219 Additionally, with the mean amount of adsorption sites estimated for each clay dispersion, a
220 K_D value normalized to the amount of sites ($K_{D,sites}$) was calculated. The relationship between
221 the mass-normalized (K_D), the sites-normalized values ($K_{D,sites}$) and the amount of sites in one
222 clay dispersion ($[Sites]$) is given by equation 2:

$$223 \quad \log K_{D,sites} \text{ (dm}^3\text{/mol of sorption sites)} = \log K_D \text{ (dm}^3\text{/kg)} - \log[Sites] \text{ (mol/kg)} \quad (2)$$

224 As mentioned above, the montmorillonite dispersions (S0 and S1) containing the largest sized
225 clay particles contain a mixture of colloidal sizes. In these dispersions, the larger clay
226 particles sediment with time, whereas the smaller clay colloids will remain suspended.
227 Therefore, a better evaluation of RN adsorption onto different colloid sizes could be made in
228 these dispersions if the average K_D value was compared to the K_D value for the particulates
229 (settled, large particles) in the clay dispersion, i.e. $K_{D,part}$, defined as:

$$230 \quad K_{D,part} = \frac{[RN]_{Tot} - [RN]_{free} - [RN]_{colloid}}{[RN]_{free}} \cdot \frac{1}{m_{part}} \quad (dm^3/kg) \quad (3)$$

231 where $[RN]_{colloid}$ is the amount of RNs associated to stable, suspended clay colloids and
232 m_{part} the amount of clay particulates.

233

234 **2.5 Geochemical speciation modelling**

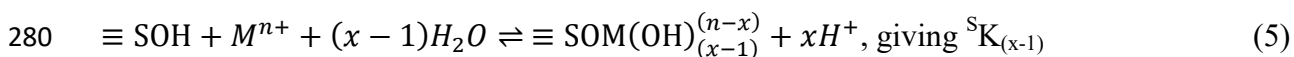
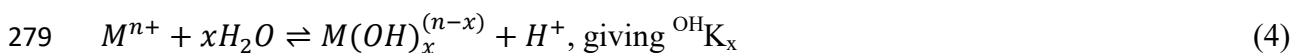
235 Predominance diagrams were plotted with PhreePlot (Kinniburgh and Cooper, 2009), which
236 contains an embedded version of the geochemical speciation program PHREEQC (Parkhurst
237 and Appelo, 1999). Stability constants for dissolved species and solubility calculations were
238 included in the NEA database (U/Np/Pu: (Guillaumont and Mompean, 2003), Tc: (Rard,
239 1999), Th: (Rand et al., 2009)). Fluoride and carbonate complexes for all RNs were
240 considered in the calculations. However, at the present chemical conditions, the fluoride
241 complexes did not play a significant role for the speciation. The formation constants of
242 $\text{Pu}(\text{OH})_2(\text{CO}_3)_2^{2-}$ and $\text{Np}(\text{OH})_2(\text{CO}_3)_2^{2-}$ selected by THEREDA (Release 2013-08-02) were
243 used in all calculations. The selected constants (in the NEA and THEREDA databases) were
244 consistent with each other. The Davies equation was used for activity coefficient calculations.
245 Reduction of sulfate and CO_2 was not considered in the calculations.

246 The cation exchange capacity (CEC) was estimated to 0.87 eq/kg by Marques Fernandes et al.
247 (Marques Fernandes et al., 2012). With the available adsorption constants, preliminary tests
248 with all RNs showed that cation exchange reactions had no significant influence at pH 8.9.
249 Consequently, cation exchange reactions were neglected in the present study.

250 To predict adsorption on natural clay rocks, Bradbury and Baeyens (Bradbury and Baeyens,
251 2011) applied a linear additive model (LAM). Their “bottom-up” approach describes the
252 overall adsorption of an element to a complex mineral mixture as the sum of the amount
253 adsorbed to each single type of mineral. For bentonite, they considered montmorillonite as the
254 only adsorbent for radionuclides. In the present case, montmorillonite represents 75 wt.% of
255 MX80 bentonite. Bradbury and Baeyens developed the 2 Site Protolysis Non Electrostatic
256 Surface Complexation and Cation Exchange (2SPNE SC/CE) model for surface complexation
257 and cation exchange reactions at montmorillonite surfaces (Bradbury and Baeyens, 2005;
258 Bradbury and Baeyens, 2006). Two types of proton active sites were necessary to describe the
259 titration data, but only one type was assumed to bind cations by the model approach. The
260 cation binding sites consist of weak sites ($[\equiv\text{WOH}] = 4 \cdot 10^{-2}$ mol/kg) as well as less abundant
261 strong sites ($[\equiv\text{SOH}] = 2 \cdot 10^{-3}$ mol/kg) with identical acid-base properties. Bradbury and
262 Baeyens (Bradbury and Baeyens, 2005; Bradbury and Baeyens, 2006) determined surface
263 complexation constants for Np(V), U(VI) and Th(IV) to strong sites of montmorillonite. Due
264 to the low RN concentrations investigated in this study and the lack of RN surface
265 complexation constants for the weak sites, only the strong sites were considered as adsorption

266 sites. In solution, all RNs were predominately present as neutral or negative species due to
 267 complexation with $\text{OH}^-/\text{CO}_3^{2-}$. Marques-Fernandez et al. (Marques Fernandes et al., 2012)
 268 determined thermodynamic constants for the formation of ternary montmorillonite-U(VI)-
 269 carbonate surface complexes. Ternary montmorillonite-Np(V)-carbonate surface complexes
 270 were not observed (Turner et al., 1998). Adsorption of TcO_4^- to clays can be neglected
 271 (Guillaumont and Mompean, 2003; Ticknor et al., 1996).

272 Though added in oxidized form, Np(V) might be reduced to Np(IV) at the clay surface in line
 273 with work by Marsac et al. (Marsac et al., 2015) in the Np-illite system. Np(IV) adsorbs more
 274 strongly to minerals than the oxidized form. Surface complexation constants for Np(IV) are
 275 unknown for montmorillonite, but Bradbury and Baeyens (Bradbury and Baeyens, 2005;
 276 Bradbury and Baeyens, 2009) proposed linear free energy relationships (LFER) between
 277 cation hydrolysis constants (equation 4) and surface complexation constants (equation 5) for
 278 illite and montmorillonite within the 2SPNE SC/CE model.



281 The LFERs for montmorillonite (equation 6) and illite (equation 7) are:

$$282 \quad \log {}^{\text{S}}K_{(x-1),\text{mont}} = 8.1 + 0.90 \times \log {}^{\text{OH}}K_x \quad (6)$$

$$283 \quad \log {}^{\text{S}}K_{(x-1),\text{ill}} = 7.9 + 0.83 \times \log {}^{\text{OH}}K_x \quad (7)$$

284 Uncertainties associated to the parameters of the LFERs were omitted for simplicity.
 285 According to Marsac et al. (Marsac et al., 2015) the formation of $\equiv \text{SONp}(\text{OH})_4^-$ was required
 286 to describe Np(IV) adsorption to illite. The same might be true for montmorillonite, as in the
 287 Th(IV) case (Bradbury and Baeyens, 2005). Unfortunately, the formation constant of
 288 $\equiv \text{SOAn}(\text{OH})_4^-$ cannot be estimated by a LFER since the formation constant for the
 289 corresponding aqueous species ($\text{An}(\text{OH})_5^-_{(\text{aq})}$) was not available. Instead, the combination of
 290 equations 6 and 7 yielded an illite-montmorillonite LFER, which can be applied to Np(IV),
 291 using surface complexation constants determined by Marsac et al. (Marsac et al., 2015):

$$292 \quad \log {}^{\text{S}}K_{(x-1),\text{mont}} = 1.08 \times \log {}^{\text{S}}K_{(x-1),\text{ill}} - 0.46 \quad (8)$$

293 The Np(IV) constants were used for Pu(IV) because of their similar hydrolysis constants. By
294 analogy with Np(IV), U(IV) and Tc(IV) surface complexes might form at the montmorillonite
295 surface. However, given the lower redox potentials of the U(VI)/U(IV) and Tc(VII)/Tc(IV)
296 couples compared to Np(V)/Np(IV), reduction of U(VI) or Tc(VII) was not expected at the
297 relatively high Eh of our experiments. Thus, U(IV) and Tc(IV) adsorption to montmorillonite
298 was not further considered.

299 Bradbury and Baeyens (Bradbury and Baeyens, 2005) showed that cations with different
300 chemical behavior (related to their oxidation state) do not compete for the same adsorption
301 sites, and have to be modelled by considering several types of binding sites for the different
302 RNs. The different sites were given the same surface site density. The tetravalent RNs Th(IV),
303 Np(IV) and Pu(IV) were expected to compete for the same strong sites. Applying the concept
304 further, Np(V) and U(VI) have no competitor for their respective sites in our study. The
305 natural occurrence of ^{238}U , was not taken into account in the calculations, which apply only to
306 the ^{233}U added to the clay dispersions. The surface complexation reactions and constants used
307 in the modeling is presented in the Supporting Information (SIF -1), Table S1.

308 Our simulations were based on the estimations and assumptions discussed above. In addition,
309 the impact of carbonates on the adsorption of most RNs onto clays has not been investigated.
310 For instance, the potential formation of ternary carbonate-RN-surface complexes, as observed
311 for U(IV) (Marques Fernandes et al., 2012) cannot be generally taken into account.

312

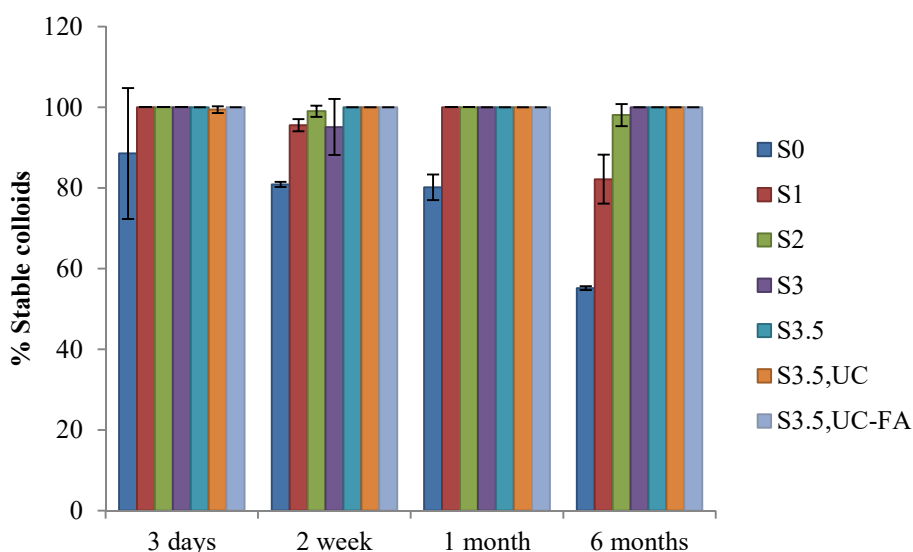
313 **3 Results and Discussion**

314 **3.1 Batch adsorption results**

315 **3.1.1 Stability of montmorillonite colloids**

316 The montmorillonite colloidal stability was followed via the evolution of the suspended Al-
317 concentration at a given time, relative to the initial Al-concentration. The percentage of stable
318 colloids for the different dispersions after 3 days, 2 weeks, 1 month and 6 months is shown in
319 Figure 3. No significant sedimentation was observed after 3 days in any dispersion except in
320 those containing larger montmorillonite colloids, i.e. S0 and S1. Here, a clear sedimentation
321 was observed at longer times (e.g. only 55% and 82% remain suspended after 6 months for
322 the dispersions S0 and S1, respectively). In previous work (Norrfors et al., 2015), the long

323 term stability of the undiluted clay dispersions were studied. In that study, 43% and 70% of
 324 the colloids remained stable in dispersions S0 and S1 after 2 months without shaking
 325 (Norrfors et al., 2015). Similar trends were found here even though the dispersions were
 326 diluted to 20 mg/L. Interestingly, the colloidal dispersion obtained after sequential (ultra-)
 327 centrifugation (S3.5) and the dispersion obtained from one direct ultra-centrifugation step
 328 (S3.5^{UC}), have a similar size distribution (Norrfors et al., 2015), showing the same high
 329 colloidal stability (Figure 3).



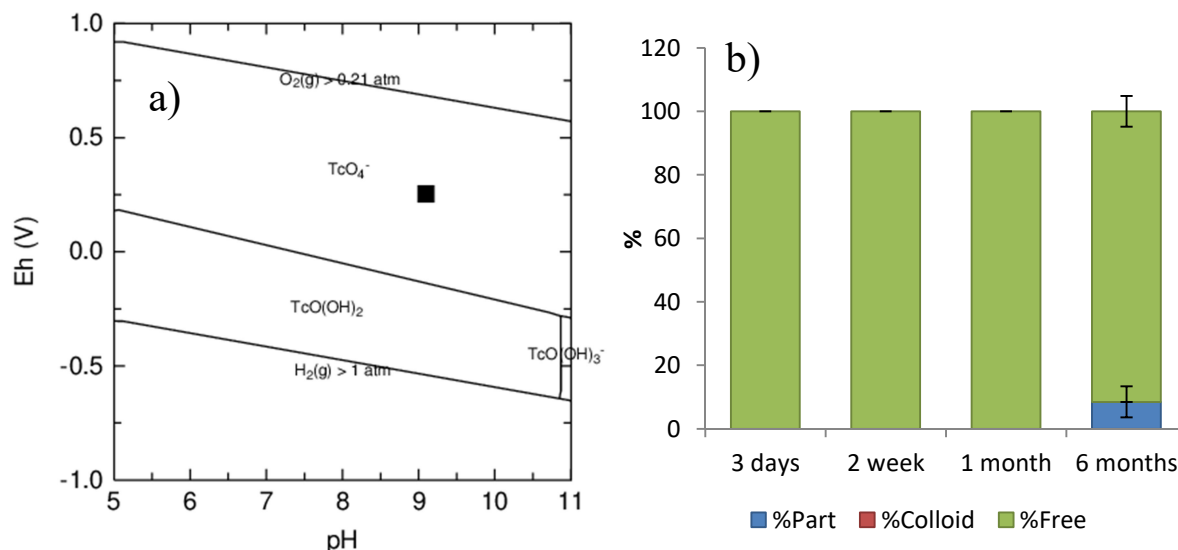
330
 331 **Figure 3: The amount of stable montmorillonite colloids in the seven clay dispersions (Table 1) as a**
 332 **function of time.**

333
 334 **3.1.2 Technetium adsorption**

335 Figure 4a shows the predominance pH-Eh diagram for Tc in solution, calculated using
 336 Phreeplot. The pH-Eh conditions measured at the end of the experiment (after 6 months, pH =
 337 8.9 ± 0.3 and Eh = 230 ± 50 mV) are shown as a black square and were clearly in the stability
 338 field of Tc(VII) (i.e. TcO_4^- (aq)). Based on this, no reduction of Tc(VII) to Tc(IV) was
 339 expected. In addition, no adsorption of Tc was expected due to the low solid to liquid ratio
 340 investigated and because of weak adsorption of TcO_4^- (aq) onto mineral surfaces (Guillaumont
 341 and Mompean, 2003; Huber et al., 2011; Ticknor et al., 1996). Figure 4b presents the
 342 distribution of Tc between particulates, suspended colloids and soluble species for the S0
 343 dispersion as a function of equilibration time. Similar results were obtained for all dispersions
 344 containing various clay size fractions, as presented in the Supporting Information (SIF -2,

345 Figure S1). The concentration of Tc(VII) remains constant in solution up to 6 months for all
 346 dispersions (Figure 4b and SIF -2, Figure S1). This supports the above statements that no
 347 reduction of technetium or adsorption onto clay colloids occurs within the analytical
 348 uncertainties, as expected from the speciation calculations. Slow reduction of Tc(VII) to
 349 Tc(IV) in presence of synthetic or Febex montmorillonite colloids has previously been noted
 350 in natural groundwater of similar low ionic strength (~1 mM) and pH = 9 after 1 month
 351 (Huber et al., 2015), which was related to the observed decrease in Eh to approximately -200
 352 mV after 1 month.

353 Since most FA remains free in dispersion (section 2.4), no distinction between Tc-FA
 354 complexes and soluble species of Tc could be done and the Tc distribution in S3.5, S3.5^{UC,FA}
 355 and S3.5^{UC} was identical, as expected (SIF -2, Figure S1).



356
 357 **Figure 4: a) Predominance pH-Eh diagram for technetium where the chemical conditions in our study**
 358 **(pH = 8.9 and Eh = 230 mV) are indicated by a black square. b) The distribution of Tc, in percentage,**
 359 **between particulates (%Part, blue), stable clay colloids (%Colloid, red) or soluble species (%Free, green)**
 360 **in the S0 dispersion is shown for different equilibration times. Histograms with the Tc distribution for the**
 361 **other clay dispersions are presented in the Supporting Information (SIF-2, Figure S1).**

362

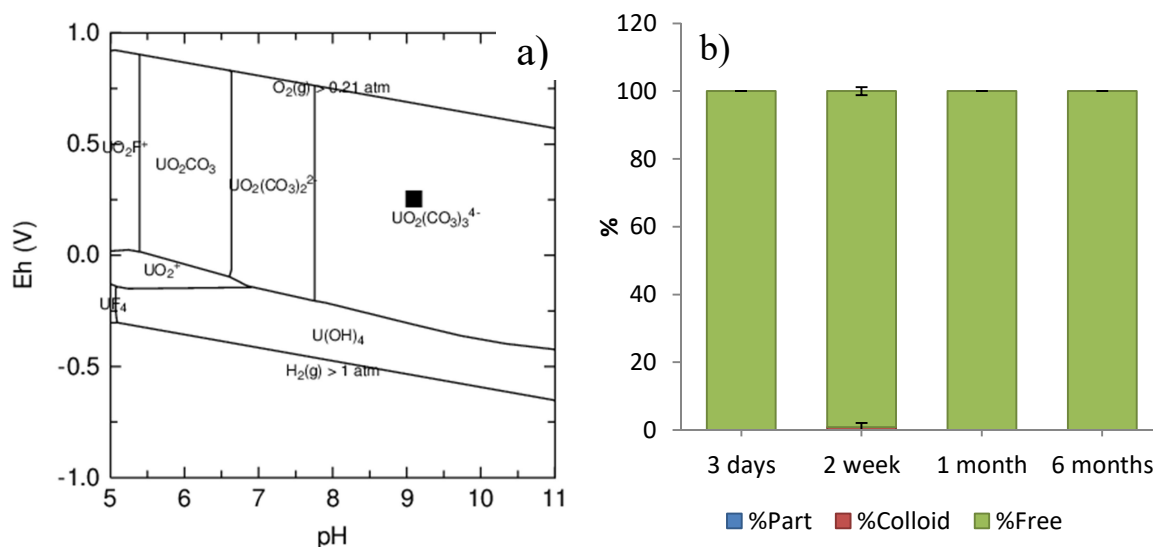
363 3.1.3 Uranium adsorption

364 In the pH-Eh predominance diagram for uranium (Figure 5a) the present experimental
 365 conditions (pH = 8.9 ± 0.3 and Eh = 230 ± 50 mV) are indicated by a black square. Due to the
 366 presence of carbonate in the SGW, uranium should be mainly present as $UO_2(CO_3)_3^{4-}$ (aq).

367 U(VI) is known to form highly soluble complexes with carbonate at pH 9 (Bernhard et al.,
 368 2001; Bradbury and Baeyens, 2011; Hartmann et al., 2008; Marques Fernandes et al., 2012;
 369 Regenspurg et al., 2009). In previous studies (Marques Fernandes et al., 2012), a log (K_D
 370 (dm^3/kg)) value of 2.7 was presented for U(VI) adsorption onto montmorillonite in 1 mM
 371 HCO_3^- and 0.1 M NaClO_4 at pH 9. This corresponds to an uptake of 1% uranium with our low
 372 clay concentration (20 mg/L). Our simulation for the SGW also predicts $\sim 1\%$ uptake. In
 373 Figure 5b, the experimental uranium adsorption for dispersion S0 is presented as the
 374 distribution of U between particulates, suspended colloids and soluble species as a function of
 375 equilibration time. The results for the other clay dispersions are presented in the Supporting
 376 Information (SIF -3, Figure S2). No uranium (^{233}U) adsorption onto montmorillonite was
 377 detected, within the experimental uncertainties, in any clay dispersions at any equilibration
 378 time. Instead, in line with published studies (Marques Fernandes et al., 2012) and model
 379 predictions, uranium remains as soluble carbonate complexes in all clay dispersions. Since FA
 380 does not strongly adsorb onto montmorillonite at pH 8.9, the results for dispersion S3.5^{UC,FA}
 381 were not expected to differ from those for dispersions in absence of FA, which agrees with the
 382 distribution presented (SIF -3, Figure S2).

383 Interestingly, a significant release of naturally occurring ^{238}U in the raw MX80 clay was
 384 observed in all dispersions (SIF-4, Figure S3). This was a consequence of the presence of
 385 carbonates in the SGW. This observation further strengthens the assumption that soluble U-
 386 carbonate complexes were the favoured species under the present chemical conditions.

387



388

389 **Figure 5: a) Predominance pH-Eh diagram for uranium in the SGW, where the chemical conditions are**
390 **indicated by a black square (pH = 8.9 and Eh = 230 mV). b) The distribution of U, in percentage, between**
391 **particulates (%Part, blue), stable clay colloids (%Colloid, red) or soluble species (%Free, green) in the S0**
392 **dispersion, shown for different equilibration times. The results obtained for the other clay dispersions are**
393 **presented in the Supporting Information (SIF -3, Figure S2).**

394

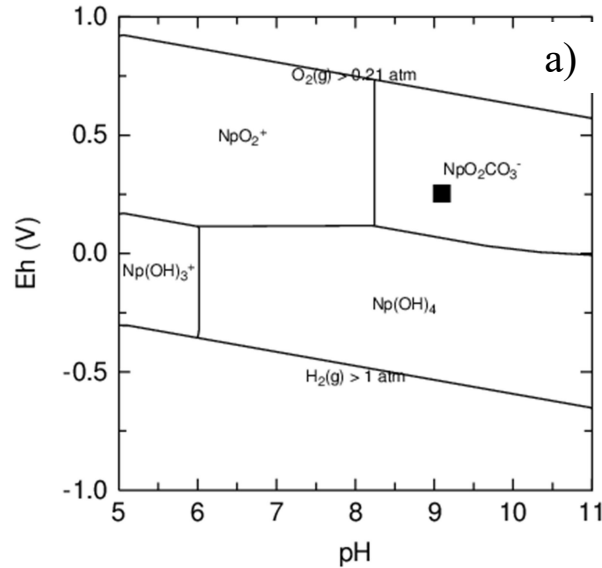
395 **3.1.4 Neptunium adsorption**

396 According to the pH-Eh predominance diagram (Figure 6a), Np should prevail as Np(V) as
397 $\text{NpO}_2\text{CO}_3^-$ in the SGW (pH = 8.9 and Eh = 230 mV) and remain in solution due to weak
398 Np(V) uptake onto montmorillonite (Missana and Geckeis, 2006; Turner et al., 1998; Wu et
399 al., 2009). The Np distribution in the S0 dispersion is presented in Figure 6b for different
400 equilibration times. The results for the other clay dispersions can be found in the Supporting
401 Information (SIF -5, Figure S4). Overall, as expected, no Np uptake on montmorillonite was
402 detected for any clay dispersion and equilibration time.

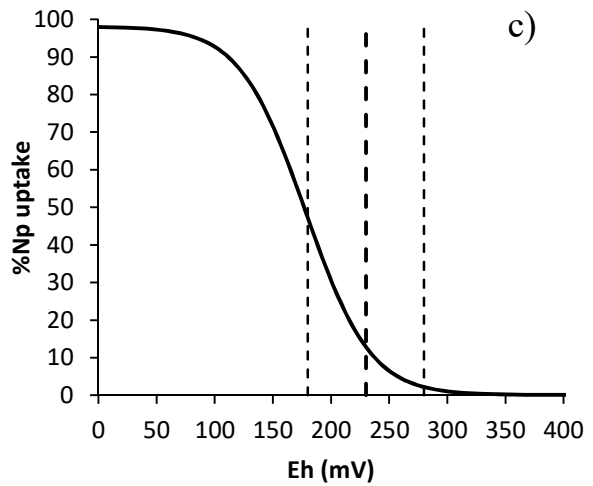
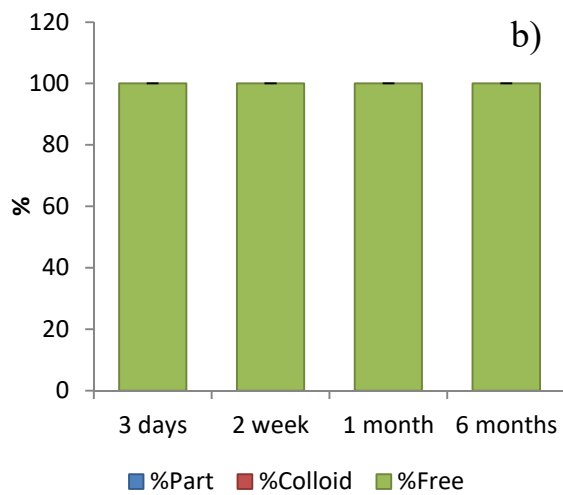
403 Recently, surface induced reduction of Np(V) to Np(IV) in the presence of illite has been
404 evidenced (Marsac et al., 2015). Although Np(V) prevailed in solution, its reduction to
405 Np(IV) was shown to be thermodynamically favoured at the illite surface due to strong
406 Np(IV) adsorption. Structural Fe(II) in illite was suspected to be the redox partner, and Fe(II)
407 is also present in our montmorillonite (Holmboe et al., 2012). Therefore, surface induced
408 reduction of Np(V) to Np(IV) might also be relevant in the case of montmorillonite. Figure 6c
409 shows the predicted percentage of Np uptake by montmorillonite as a function of Eh in the
410 SGW at pH 8.9. For Eh < 50 mV, Np(IV) prevails both at the surface and in solution, leading
411 to nearly complete Np uptake by montmorillonite. For Eh > 300 mV, Np(V) prevails both at
412 the surface and in solution and no uptake was predicted. For 50 < Eh < 300 mV, Np(V)
413 prevails in solution whereas Np(IV) prevails at the surface, leading to an intermediate
414 behaviour, which is highly sensitive to changes in Eh. The measured Eh (+230 mV) is shown
415 as a dashed line, with the experimental uncertainty (± 50 mV), as dotted lines in Figure 6c.
416 The model predicts an uptake of approximately 10% Np at pH 8.9 and $E_{h(\text{SHE})} = +230$ mV.
417 However, given the uncertainties in (i) the experimental Eh value and (ii) Np(IV) surface
418 complexation constants reported in the 2 SPNE SC/CE model (Marsac et al., 2015), the
419 experimental Np uptake was qualitatively consistent with the predictions.

420 As for U and Tc, the presence of FA in S3.5^{UC,FA} did not change the Np uptake as expected,
 421 since FA remains predominantly in solution (SIF -5, Figure S4).

422



423



424

425 **Figure 6: a) Predominance pH-Eh diagram for Np in the SGW. The black square corresponds to the**
 426 **present experimental conditions (pH = 8.9 and Eh = 230 mV). b) Histograms presenting the distribution of**
 427 **neptunium, in percentage, between particulates (%Part, blue), stable colloids (%Colloid, red) or soluble**
 428 **species (%Free, green) in the S0 dispersion shown for different equilibration times. Histograms with the**
 429 **Np distribution for the other clay dispersions are presented in the Supporting Information (SIF -5, Figure**
 430 **S4). c) Predicted percentage uptake of Np by bentonite in the SGW as a function of Eh at pH 8.9. The**
 431 **experimental Eh (230 ± 50 mV) is shown as dashed lines.**

432

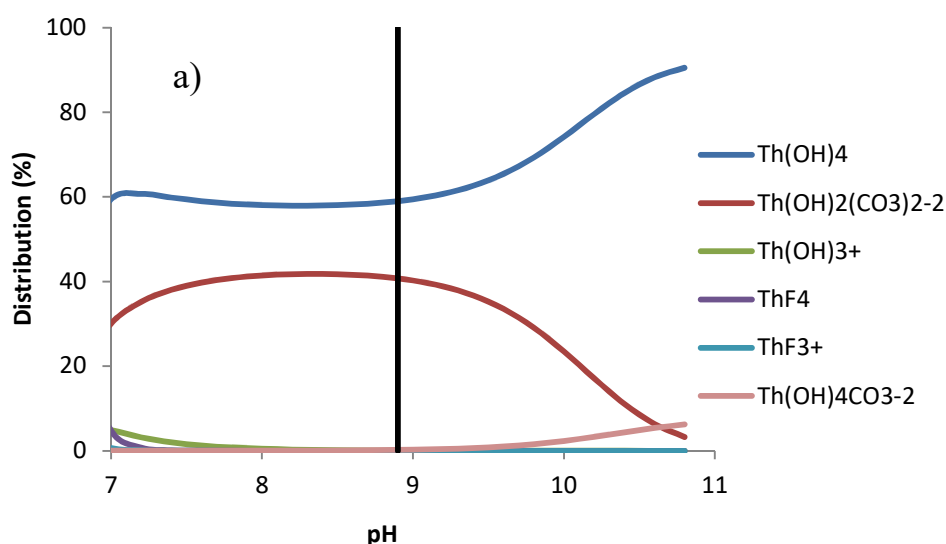
433 3.1.5 Thorium adsorption

434 The Th speciation in the SGW is shown as a function of pH in Figure 7a. Th was predicted to
435 be present as $\text{Th}(\text{OH})_{4(\text{aq})}$ (60%) and $\text{Th}(\text{OH})_2(\text{CO}_3)_2^{2-}$ (40%) at pH 8.9, marked as a vertical
436 line in Figure 7a. Accordingly, the model predicts 83% of Th(IV) uptake onto
437 montmorillonite, corresponding to $\log(K_D (\text{dm}^3/\text{kg})) = 5.4$. The distribution of Th in the S0
438 dispersion between particulates, suspended colloids or soluble species as a function of
439 equilibration time is presented in Figure 7b. The results for the other clay dispersions are
440 presented in the Supporting Information (SIF -6, Figure S5). Thorium was strongly adsorbed
441 in all clay dispersions. The amount of settled Th increases with time in S0 (Figure 7b). This
442 follows the increase in the amount of depositing clay particles, as already mentioned (Figure
443 3), pointing to the association of a fraction of Th with those unstable, large montmorillonite
444 particulates. For the clay dispersions containing smaller sized colloids (S2→S3.5^{UC}), no
445 sedimentation was expected which was in line with the experimental results, especially as
446 small amounts of particulates found in all dispersions could rise from artefacts (e.g.
447 adsorption to walls), as this fraction was not measured directly (but calculated from the total
448 amount Th subtracting the measured amounts of Th in colloidal and aqueous phases).

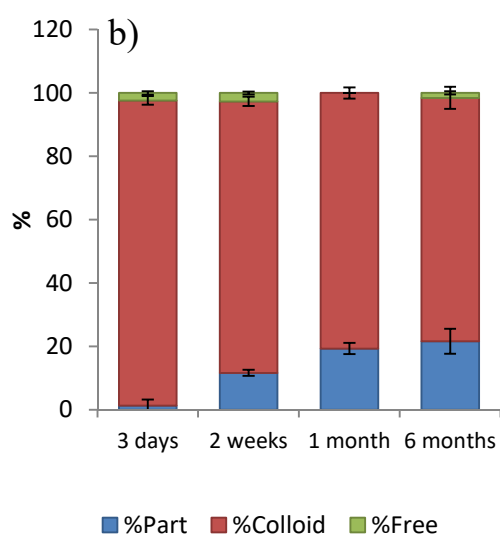
449 The K_D values calculated for Th in the different clay dispersions are presented as a function of
450 equilibration time in Figure 7c. Data points for samples where the concentration of Th as
451 soluble species were below the detection limit are not shown. Nevertheless, no significant
452 variations in Th uptake was found. Overall, no kinetic effects were observed. Our $\log(K_D$
453 $(\text{dm}^3/\text{kg})) = 6.4 \pm 0.5$ were similar to those previously observed. $\log(K_D (\text{dm}^3/\text{kg})) = 6.4 \pm$
454 0.5 and $\log(K_D (\text{dm}^3/\text{kg})) = 5.3 \pm 0.5$ for batch adsorption experiments were reported by
455 Huber et al. (Huber et al., 2011; Huber et al., 2015) and Bouby et al. (Bouby et al., 2011),
456 respectively, in a low ionic strength (~1 mM) groundwater at pH = 8.3 - 9.5 at carbonate
457 concentrations of ~0.05 mM, comparable to the SGW used in our study. The experimental K_D
458 value was slightly higher than expected from modelling (dashed line in Figure 7c).
459 Nevertheless, the model for Th(IV) uptake was calibrated with the experimental results of
460 Bradbury and Baeyens (Bradbury and Baeyens, 2005), involving a measured $\log(K_D$
461 $(\text{dm}^3/\text{kg})) \approx 5.5$ for Th at pH = 9 in 0.1 M NaClO_4 , i.e. in higher ionic strength and in absence
462 of carbonate.

463 In the montmorillonite dispersion obtained in presence of FA (S3.5^{UC,FA}), the Th uptake onto
464 clay colloids was significantly lower compared to the dispersions in absence of organic matter

465 (S3.5^{UC}, Figure 7c and SIF -6, Figure S5). Log (K_D (dm³/kg)) was reduced to 5.3 ± 0.5 and
 466 remains constant over time (Figure 7c). FA form complexes with Th(IV) which compete with
 467 Th-montmorillonite surface complexes. This K_D value corresponded to a decrease in the
 468 amount of adsorbed Th by approximately 15% (see histograms in the Supporting Information,
 469 SIF -6, Figure S5). Pan et al. (Pan et al., 2011) reported a decrease in log (K_D (dm³/kg)) from
 470 ~ 6.0 to ~ 5.4 after addition of FA in absence of carbonate, at pH = 9 and in 50 mM NaCl, with
 471 a FA to Na-bentonite ratio of 1:5 compared to 1:10 in our study. Yu et al. (Yu et al., 2008)
 472 reported an even larger decrease in log (K_D (dm³/kg)) value in presence of FA (from ~ 5.2 to
 473 ~ 3.9) with a FA to bentonite ratio of 1:30 at pH = 9, at slightly higher ionic strength (0.1 M
 474 NaNO₃). Therefore, the present results were in line with literature data.

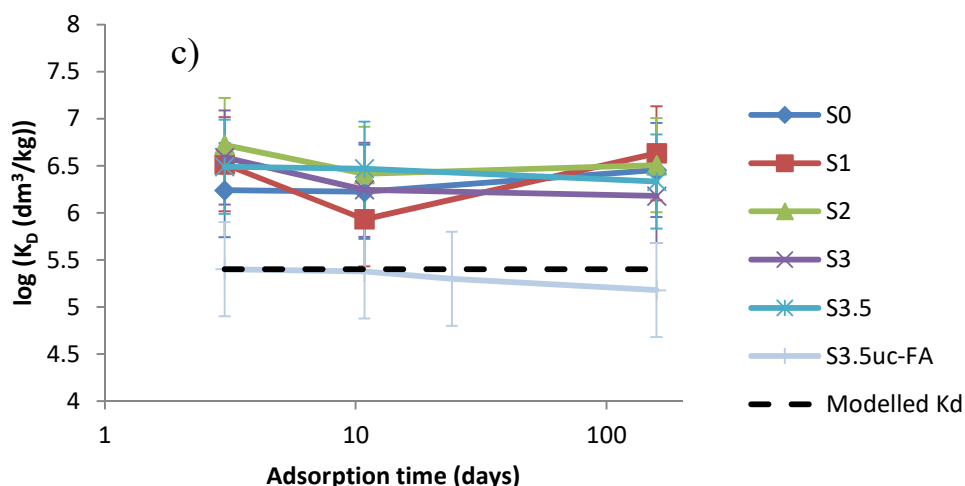


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478

479 Figure 7: a) Species distribution diagram for thorium as a function of pH in the SGW. The experimental
 480 pH = 8.9 is marked as a vertical line. b) Histograms presenting the distribution of Th, in percentage,
 481 between particulates (%Part, blue), stable clay colloids (%Colloid, red) or soluble species (%Free, green)
 482 in the S0 dispersion, shown for different equilibration times. The results obtained for the other clay
 483 dispersion are presented in the Supporting Information (SIF -6, Figure S5). c) Adsorption of Th for all
 484 different sized montmorillonite dispersions, expressed as log (K_D (dm³/kg)) values as a function of
 485 equilibration time. The dashed line corresponds to the predicted Th adsorption from modelling.

486

487 3.1.6 Plutonium adsorption

488 In the predominance pH-Eh diagram for Pu (Figure 8a), the experimental conditions are
 489 marked by a black square (pH = 8.9 and Eh = 230 mV). In the SGW, Pu was expected to
 490 prevail as Pu(IV) mainly as Pu(OH)₂(CO₃)₂²⁻_(aq). Pu(IV) is known to adsorb strongly onto
 491 montmorillonite (Geckeis et al., 2004; Latrille et al., 2006; Lujanienė et al., 2007). Even
 492 though the total amount of Pu would exceed the solubility limit of Pu(IV) (Huber et al., 2011),
 493 the final aqueous Pu concentration was below the saturation with respect to PuO_{2(am,hydr)}
 494 because of the strong adsorption of Pu onto montmorillonite. Furthermore, since adsorption is
 495 usually a faster process than nucleation and precipitation, precipitation of Pu was not expected
 496 (Zhao et al., 2011). An uptake of 97% Pu(IV) was predicted by the model. This was
 497 consistent with the simulated Np uptake at Eh < 50 mV (see Figure 6c), where Np(IV) would
 498 prevail both at the surface and in solution. A Pu uptake of 97% corresponds to log (K_D
 499 (dm³/kg)) = 6.3 in our experimental conditions.

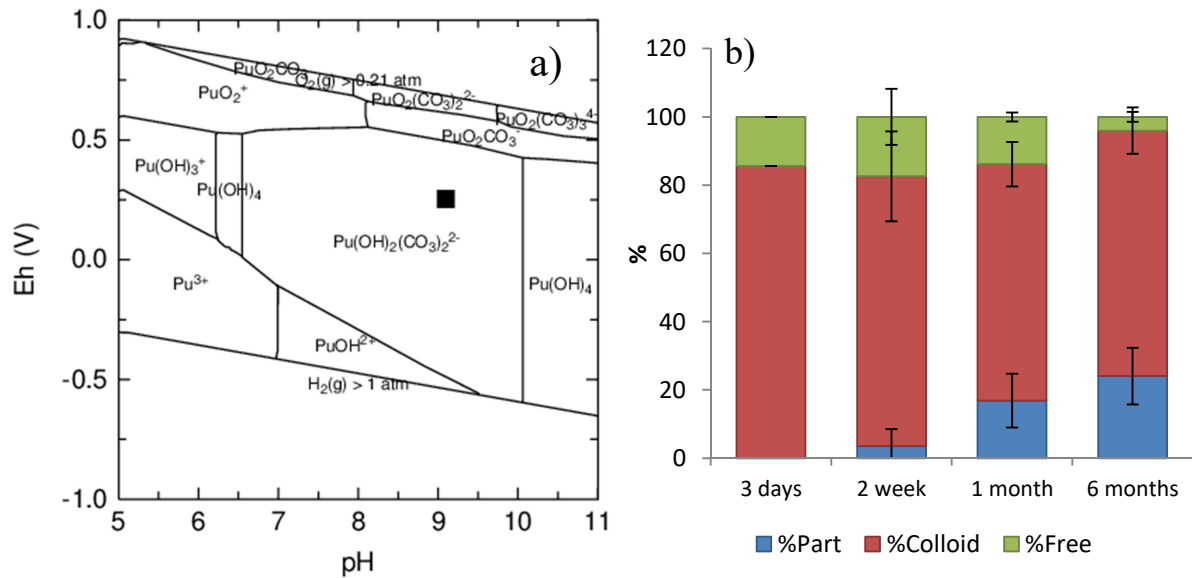
500 The distribution of Pu as a function of equilibration time is presented for the clay dispersion
 501 S0 in Figure 8b. Pu was largely associated to montmorillonite. The distribution of Pu in the

502 other clay dispersions is presented in the Supporting Information and was comparable to the
503 results found for S0 (SIF -7, Figure S6 and Figure 8b). As for Th, some Pu is associated to
504 particulates present in the clay dispersions with the largest colloids (i.e. S0 and S1) which is
505 seen over time). This was explained by sedimentation of larger montmorillonite particles (see
506 Figure 3). In the dispersion with smaller colloids, no Pu particulates were found (SIF -7,
507 Figure S6). K_D values for Pu adsorption to each clay suspension are presented as a function of
508 equilibration time in Figure 8c. Pu uptake does not significantly evolve over the first month,
509 with an average distribution coefficient for all dispersions of $\log(K_D \text{ (dm}^3/\text{kg)}) = 5.7 \pm 0.5$.
510 Although, the Pu(IV) surface complexation constants for the 2 SPNE SC/CE model used in
511 this study were based on several approximations, the predicted $\log(K_D \text{ (dm}^3/\text{kg)}) = 6.3$
512 (dashed line in Figure 8c) agrees well with the experimental data. High uptake of Pu show
513 that Pu(IV) predominated in the SGW. However, the uptake was slightly lower than for Th
514 (Figure 7c) and the slight increase in uptake of Pu over time (almost insignificant given the
515 error bars) might suggest the presence of a small fraction of Pu(III), as present initially, which
516 took time to oxidize to Pu(IV). After 6 months equilibration time, the uptake of Pu was
517 similar to those reported for Th and those predicted from the model. They indicate a
518 consistent high adsorption of the two tetravalent RNs. Previous studies (Geckeis et al., 2004;
519 Huber et al., 2015) reported $\log(K_D \text{ (dm}^3/\text{kg)}) = 5.4 \pm 0.5$ and $\log(K_D \text{ (dm}^3/\text{kg)}) = 6.4 \pm 0.5$
520 in ground waters of low ionic strength (~ 1 mM) and $\text{pH} = 9.5 - 9.6$ for adsorption of Pu(IV)
521 to montmorillonite. These values were consistent with the present work despite higher Eh in
522 our study (0 to -200 mV in (Geckeis et al., 2004; Huber et al., 2015)), due to the large stability
523 field of Pu(IV) at $\text{pH} \approx 9$.

524 As for Th, we observe a lower Pu uptake onto the clay in the S3.5^{UC,FA} dispersion since FA
525 was acting as a competing ligand (Figure 8c). Pu adsorption in the presence of FA remained
526 constant at $\log(K_D \text{ (dm}^3/\text{kg)}) = 5.1 \pm 0.5$. In previous published work, the reported
527 competitive effect of added FA differs. Thus, Ticknor et al. (Ticknor et al., 1996) investigated
528 Pu uptake by montmorillonite ($[\text{Pu(IV)}] = 1.1 \cdot 10^{-10}$ M, $m/V = 25$ g/L) in the presence of FA
529 (0 – 4.84 mg/L) at $\text{pH} = 7.7$, with 56 mg/L HCO_3^- and an ionic strength of ~ 0.2 M, and
530 observed a maximum decrease in $\log(K_D \text{ (dm}^3/\text{kg)})$ from ~ 4.8 to ~ 3.5 , even though their FA
531 to montmorillonite ratio was far less than in our study. On the opposite, Boggs et al. (Boggs et
532 al., 2015) did not find any effect of FA addition at $\text{pH} = 8$ in 0.01 M NaCl. In that study, the
533 FA to montmorillonite ratio was higher ($m/V = 0.1$ g/L, $[\text{FA}] = 1.5$ mg/L, $[\text{Pu(IV)}] = 10^{-10}$
534 M). A decrease in Pu adsorption was expected under our conditions as suggested by the Th

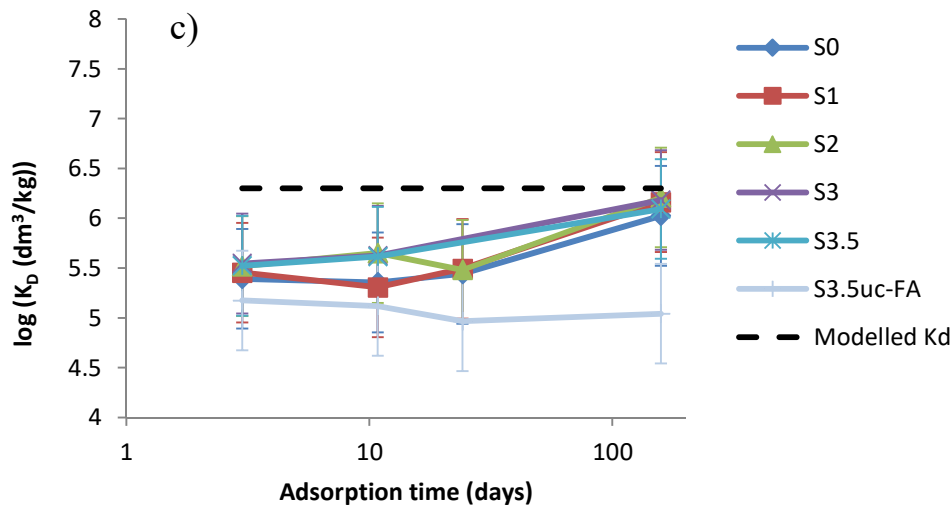
535 results (Figure 7c) and similar studies with gibbsite, FA and Pu(IV) at pH 8 – 10 in 0.1 M
 536 NaCl (Simpkins, 2011).

537



538

539



540

541 **Figure 8:** a) Predominance pH-Eh diagram for Pu in the SGW. The experimental conditions are marked
 542 by a black square (pH = 8.9 and Eh = 230 mV). b) Histograms presenting the distribution of Pu, in
 543 percentage, between particulates (%Part, blue), stable clay colloids (%Colloid, red) or soluble species
 544 (%Free, green) in the S0 dispersion, shown for different equilibration times. The results obtained for the
 545 other clay dispersions are presented in the Supporting Information (SIF -7, Figure S6). c) Adsorption of
 546 Pu for all different sized montmorillonite dispersions, expressed as log (K_D (dm^3/kg)) values as a function
 547 of equilibration time. The dashed line corresponds to the predicted Pu adsorption from modelling.

549 **3.2 Discussion of colloidal size effect on adsorption of RNs onto montmorillonite**

550 The present batch adsorption results do not suggest that any of the tested clay colloid
551 dispersions particularly favour adsorption of Th(IV) and Pu(IV), within the analytical
552 uncertainties (see Figures 7c and 8c where the uptake of Th and Pu was normalized to the
553 mass of montmorillonite and expressed as $\log K_D$ according to equation 1). To better compare
554 the amount of adsorbed RNs, the estimated amounts of edge sites were calculated by
555 assuming disc-shaped particles with a given mean particle size (Norrfors et al., 2015). The
556 estimates for each clay dispersion are included in Table 1, which suggests an increase by a
557 factor of approximately six in the amount of sites (corresponding to both weak and strong
558 sites according to the 2 SPNE SC/CE model) between the dispersions containing all the clay
559 particle sizes (S0) and those more restricted to smaller sizes (S3.5^{UC}). Based on these
560 estimations, a factor six difference in the amount of adsorbed RNs could be expected. K_D
561 values normalized to the amount of sites ($K_{D,sites}$), instead of mass, could be calculated using
562 equation 2. This yielded a maximal theoretical difference of $\log(6) = 0.8$ units between the
563 two dispersions S0 and S3.5. Nevertheless, this value was similar to the experimental
564 uncertainty (± 0.5 units) for $\log K_D$ measurements, and could explain why no significant
565 difference in adsorption between the clay dispersions could be detected in our study.

566 To better compare the adsorption onto smaller and larger clay colloids, K_D values for the
567 montmorillonite pertaining to the particulate phase ($K_{D,part}$, for the larger particles) were
568 calculated, using equation 3. This $K_{D,part}$ value can be compared to the K_D value of stable,
569 suspended montmorillonite colloids (corresponding to smaller colloids). All clay dispersions
570 were polydisperse and in the dispersions with the largest sized colloids, the smaller sized
571 colloids were present as well. From the amount of settled colloids (Figure 3), compared to the
572 amount of Th in the particulate phase in dispersion S0 after 6 months (Figure 7b), a log
573 ($K_{D,part} \text{ (dm}^3/\text{kg)}) = 6.2 \pm 0.5$ was obtained. This was similar to $\log (K_D \text{ (dm}^3/\text{kg)}) = 6.3 \pm 0.5$
574 obtained for the smaller, stable dispersion S3.5, within the experimental uncertainties.
575 Consequently, the amount of adsorbed Th was similar for both clay dispersions and no
576 difference in K_D values related to the mean colloidal size in the clay dispersions could be
577 inferred.

578 To summarize, no significant differences between adsorption of strongly adsorbing RNs onto
579 the smallest and largest sized montmorillonite colloids could be deduced, so that an “average

580 $\log(K_D)$ ” should provide sufficient estimates for RN adsorption to bentonites. This “average
581 $\log(K_D)$ ” can be used in reactive transport modelling with confidence, which simplifies
582 models for RN migration accordingly. To better study a potential effect of colloidal size, one
583 may recommend the use of RNs which adsorb to clays stronger than penta- hexa- and
584 heptavalent RNs but weaker than tetravalent RNs.

585 While an ultimate statement concerning desorption properties related to the mean colloidal
586 (particle) size for the added RNs cannot be made, an effect did occur for natural ^{238}U which
587 varied significantly with the clay dispersion properties (see Supporting Information, SIF-4).

588

589 **4 Conclusions**

590 In this work, experiments were performed on RN uptake onto size separated montmorillonite
591 colloids. Np(V), Tc(VII) and U(VI) were found not to adsorb onto montmorillonite under the
592 present experimental conditions. Instead, they were present as soluble species, mainly as
593 $\text{NpO}_2\text{CO}_3^-$ (aq), TcO_4^- (aq) and $\text{UO}_2(\text{CO}_3)_3^{4-}$ (aq), respectively. On the contrary, Th(IV) and Pu(IV)
594 strongly adsorb onto montmorillonite. If fulvic acids are present (as here during the
595 fractionation step of the clay colloids and after the dilution of their dispersions), the amount
596 Pu and Th associated with clay was significantly decreased. During the experimental
597 observation period (up to 6 months), larger clay particles settled with time. A part of Th and
598 Pu were adsorbed and remain adsorbed on these larger, unstable montmorillonite particles
599 (i.e. in the particulate phase). All experimental results were in line with model predictions.

600 No difference in adsorption behaviour of Th and Pu onto different sized clay colloids,
601 expressed as mass-normalized K_D values, was found. Between the clay dispersions with
602 smallest and the largest mean colloidal sizes, an estimated difference by a factor of six in the
603 amounts of edge sites was calculated. This was too small to be detectable within the
604 experimental uncertainties. Therefore, based on the experimental results for MX-80 presented
605 here, it seems to be valid to implement an “average $\log K_D$ ” for all colloidal sizes in reactive
606 transport modelling codes.

607 While a variation in the montmorillonite colloidal size does not seem to influence the
608 adsorption behaviour of strongly adsorbing RNs, the question remains if it affects RN
609 desorption and desorption kinetics. This is presently investigated in a separate study.

610

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