

Effect of Ca(II) on U(VI) and Np(VI) retention on Ca-bentonite and clay minerals at hyperalkaline conditions – New insights from batch sorption experiments and luminescence spectroscopy

Philipp, T.; Huittinen, N. M.; Shams Aldin Azzam, S.; Stohr, R.; Stietz, J.; Reich, T.; Schmeide, K.;

Originally published:

June 2022

Science of the Total Environment 842(2022), 156837

DOI: <https://doi.org/10.1016/j.scitotenv.2022.156837>

Perma-Link to Publication Repository of HZDR:

<https://www.hzdr.de/publications/Publ-34369>

Release of the secondary publication
on the basis of the German Copyright Law § 38 Section 4.

CC BY-NC-ND

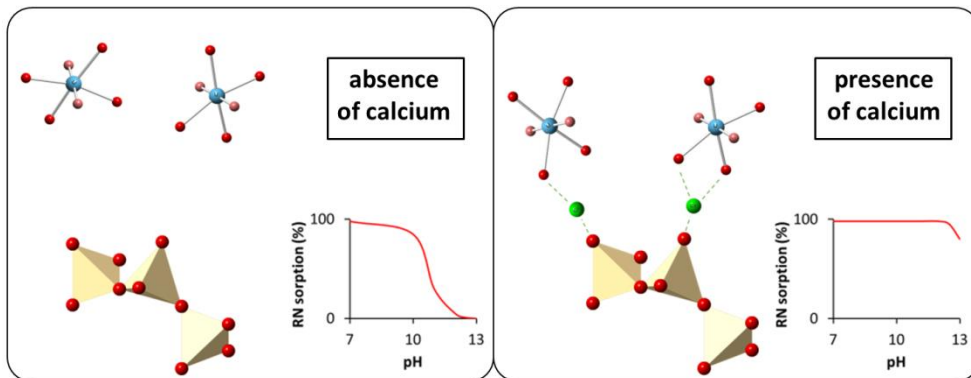
1 **Effect of Ca(II) on U(VI) and Np(VI) retention on Ca-bentonite and clay minerals at**
2 **hyperalkaline conditions – New insights from batch sorption experiments and**
3 **luminescence spectroscopy**

4 Thimo Philipp ^{a,1}, Nina Huittinen ^a, Salim Shams Aldin Azzam ^a, Robin Stohr ^b, Janina Stietz ^b, Tobias
5 Reich ^b, Katja Schmeide ^{a,*}

6

7 ^a Helmholtz-Zentrum Dresden – Rossendorf e.V., Institute of Resource Ecology, Bautzner Landstraße
8 400, 01328 Dresden, Germany

9 ^b Johannes Gutenberg-Universität Mainz, Department of Chemistry, Fritz Strassmann Weg 2, 55128
10 Mainz, Germany



11
12

13

14

15

16

17

18

19

20 * Corresponding author: Dr. Katja Schmeide (E-mail address: k.schmeide@hzdr.de, phone: +49 351
21 260 2436).

22 ¹ Present address: Federal Office for the Safety of Nuclear Waste Management (BASE), Wegelystraße
23 8, 10623 Berlin, Germany

24 **Abstract**

25 In deep geological repositories for radioactive waste, interactions of radionuclides with mineral
26 surfaces occur under complex geochemical conditions involving complex solution compositions and
27 high pH resulting from degradation of cementitious geo-engineered barriers. Ca^{2+} cations have been
28 hypothesized to play an important role as mediators for the retention of U(VI) on Ca-bentonite at
29 (hyper)alkaline conditions, despite the anionic character of both the mineral surface and the aqueous
30 uranyl species. To gain deeper insight into this sorption process, the effect of Ca^{2+} on U(VI) and
31 Np(VI) retention on aluminosilicate minerals has been comprehensively evaluated, using batch sorption
32 experiments and time-resolved laser-induced luminescence spectroscopy (TRLFS). Sorption
33 experiments with Ca^{2+} or Sr^{2+} and zeta potential measurements showed that the alkaline earth metals
34 sorb strongly onto Ca-bentonite at pH 8–13, leading to a partial compensation of the negative surface
35 charge, thereby generating potential sorption sites for anionic actinyl species. U(VI) and Np(VI)
36 sorption experiments in the absence and presence of Ca^{2+} or Sr^{2+} confirmed that these cations strongly
37 enhance radionuclide retention on kaolinite and muscovite at $\text{pH} \geq 10$. Concerning the underlying
38 retention mechanisms, site-selective TRLFS provided spectroscopic proof for two dominating U(VI)
39 species at the aluminosilicate surfaces: (i) A ternary U(VI) complex, where U(VI) is bound to the
40 surface via bridging Ca cations with the configuration $\text{surface} \equiv \text{Ca} - \text{OH} - \text{U(VI)}$ and, (ii) U(VI)
41 sorption into the interlayer space of calcium (aluminum) silicate hydrates (C-(A-)S-H), which form as
42 secondary phases in the presence of Ca due to partial dissolution of aluminosilicates under hyperalkaline
43 conditions. Consequently, the present study confirms that alkaline earth elements, which are
44 ubiquitous in geologic systems, enable strong retention of hexavalent actinides on clay minerals under
45 hyperalkaline repository conditions.

46

47 **Keywords:** Kaolinite, Muscovite, Uranium, Calcium bridge, C-S-H, TRLFS

48

49 1. Introduction

50 The strategy followed by many countries to ensure the long-term containment of spent nuclear
51 fuel and high-level radioactive waste is the final disposal in deep geological formations involving
52 multiple protective barriers. Therefore, it is necessary to generate a profound understanding of the
53 interactions between radionuclides (RNs) and mineral surfaces under the conditions expected in a deep
54 geological waste repository.

55 The chemical system in the near-field of a nuclear waste repository is very complex. It is
56 influenced by the presence of different materials as components of a multi-barrier system, consisting
57 of three principal parts: technical barriers (steel or copper containers enclosing the nuclear waste),
58 geotechnical barriers (e.g., bentonite, cementitious materials, asphalt/bitumen elements), and the
59 geological barrier (argillaceous, crystalline or salt host rock) (OECD/NEA, 2020). In most repository
60 concepts, bentonite, a natural swelling clay with high montmorillonite content, will be used as buffer
61 and backfill material (Jenni et al., 2019; Kaufhold and Dohrmann, 2016; Lommerzheim and Jobmann,
62 2014). Due to its good sealing properties and high sorption capacity for radiotoxic and/or chemotoxic
63 waste components, the bentonite is expected to protect and isolate the canisters containing the waste
64 and to retain and retard RNs in case of canister degradation and failure. Cementitious materials, used
65 for concrete lining and concrete plugs in the repository, are applied to ensure mechanical stability and
66 sealing of disposal tunnels and galleries.

67 Natural pore waters in deep geological formations feature a complex composition, containing
68 several cations and anions which could either form stable complexes with potentially released RNs or
69 compete with the RNs for sorption sites on available mineral surfaces. These pore waters can have
70 considerably high ionic strengths. For instance, in North German clay formations, which are
71 considered as potential host rocks, salinities of about 150 g/L are expected in the lower cretaceous
72 claystones at 800 m depth (Nowak and Maßmann, 2013; Wolfgramm et al., 2011). High salinities
73 promote the corrosion of concrete within the geotechnical barrier, leading to the evolution of
74 hyperalkaline cement pore waters ($10 < \text{pH} < 13$) (Berner, 1992; Gaucher et al., 2006) with enhanced
75 Ca^{2+} contents. The strongly increased alkalinity of contact waters in turn can lead to mineral
76 alterations of the bentonite backfill and formation of secondary phases and, moreover, can modify RN

77 speciation. Altogether, these processes can affect the RN retention potential of bentonite. Hence,
78 laboratory studies on RN sorption on mineral surfaces must preferably be conducted in consideration
79 of multi-mineral solid phases, complex solution composition, high ionic strength, high pH values and
80 low RN concentrations.

81 Most RN retention/diffusion studies with argillaceous rocks or clay minerals have been conducted
82 either at a pH representative of natural clay pore water or in the pH range of approximately 3 to a
83 maximum of 10, and predominately at low ionic strengths (Hennig et al., 2020; Joseph et al., 2017;
84 Joseph et al., 2013b; Marques Fernandes et al., 2012; Schmeide and Bernhard, 2010; Tran et al., 2018;
85 Wu et al., 2009). Only few RN retention studies were performed at increased ionic strengths (Marsac
86 et al., 2017; Nagasaki et al., 2016; Schnurr et al., 2015; Scholze et al., 2019; Stockmann et al., 2022).
87 Even less RN retention studies were performed at increased ionic strengths and hyperalkaline
88 conditions. In our recent study, U(VI) retention on Ca-bentonite was investigated in the pH range 8–13
89 and at increased ionic strength applying the so called ‘diluted Gipshut solution’ (2.5 M NaCl, 0.02 M
90 CaCl₂, 0.02 M Na₂SO₄, and 0.0051 M KCl; $I = 2.63$ M) as background electrolyte (Philipp et al.,
91 2019). Despite the fact that both the bentonite surface and the prevailing aqueous uranyl complexes
92 are negatively charged in this high pH range, the results showed a strong U(VI) retention onto Ca-
93 bentonite up to pH 12. Uranyl carbonates do not play a role at hyperalkaline conditions due to the
94 predominance of uranyl hydrolysis. The retention of U(VI) reached its maximum at conditions where
95 UO₂(OH)₃⁻ dominated the aqueous speciation. By means of site-selective TRLFS (at 10 K) and X-ray
96 absorption fine structure (EXAFS) spectroscopy, two independent U(VI) sorption species were
97 detected on Ca-bentonite at pH 8–13, whereas U(VI) precipitation was excluded. With increasing pH,
98 the nature of the retained U(VI) complexes shifted from bidentate inner-sphere surface complexes
99 with an overall equatorial coordination of five, adsorbed on aluminol or silanol edge sites, to a surface
100 complex with a 4-fold equatorial coordination, resembling the aqueous species UO₂(OH)₄²⁻.
101 Concerning the character of this latter sorption species at very high pH, it was hypothesized that the
102 binding of the anionic uranyl hydroxide complexes to the negatively charged surface is mediated by
103 Ca²⁺ cations (Philipp et al., 2019). This hypothesis was recently supported by Brix et al. (2021), who
104 observed higher U(VI) retention in hyperalkaline chemical systems with higher Ca²⁺ concentrations

105 and proposed a bridging effect of Ca^{2+} . Using calcium silicate hydrate (C-S-H) phases, which are
106 major constituents of fresh and degraded cement, as an example, Androniuk and Kalinichev (2020)
107 proposed complex formation between $\text{UO}_2(\text{OH})_3^-$ and Ca^{2+} sorbed on negatively charged silanol
108 groups based on molecular dynamics simulations. However, spectroscopic proof of the existence of
109 such complexes under hyperalkaline conditions is still missing.

110 Therefore, the focus of the present paper is the detailed study of the potential effect of Ca^{2+} on
111 U(VI) retention onto clay mineral surfaces at hyperalkaline conditions, and the unambiguous
112 description of the underlying sorption mechanisms. Consequently, the sorption of Ca^{2+} on the naturally
113 occurring clay rock Ca-bentonite and its effect on the bentonite surface charge was studied at pH 8–
114 13. In addition, to quantify the influence of Ca^{2+} on U(VI) sorption on Ca-free mineral phases, U(VI)
115 batch sorption experiments were conducted with the clay mineral kaolinite as well as with the clay
116 mineral analogue muscovite in 0.1 M NaCl as well as in 0.1 M NaCl + 0.02 M CaCl_2 at pH 8–13.
117 Furthermore, equivalent batch sorption experiments were performed in the presence of Sr^{2+} instead of
118 Ca^{2+} and with Np(VI) in order to elucidate whether the observed phenomena are similarly valid for
119 other alkaline earth metals as well as other hexavalent actinides. To address the underlying retention
120 mechanisms occurring at these clay mineral surfaces, laser-induced luminescence spectroscopy was
121 applied to identify U(VI) sorption species in the absence and presence of Ca^{2+} .

122

123 **2. Materials and methods**

124 **2.1. Materials**

125 The Ca-bentonite was of the type Calcigel® (Clariant, Munich, Germany) with a mineral
126 composition of 60–70% montmorillonite, 6–9% quartz, 1–6% mica, 1–4% feldspar, 1–2% kaolinite
127 and 5–10% others (supplier information). Particle sizes range between 0.5 and 150 μm with the
128 dominant fraction (90%) of the particles being smaller than 90 μm ; the BET specific surface area
129 (SSA) was determined to be 76.5 m^2/g (Philipp et al., 2019).

130 Synthetic kaolinite was obtained as described in Huittinen et al. (2010) by hydrothermal treatment
131 of an aluminosilica gel at 220 °C according to the procedure by Fialips et al. (2000). The SSA was

132 determined to be 22.2 m²/g. The particle size was < 1.1 μm as observed by SEM; EDX mapping
133 revealed that the synthetic kaolinite did not contain any impurities (the only elements detected were O,
134 Al and Si) (Huittinen et al., 2010). Natural kaolinite from Georgia (KGa-1b) was obtained from the
135 Source Clay Repository of the Clay Minerals Society, it was used as received. The SSA was
136 determined to be 11.7 m²/g. Its chemical and mineralogical characterization is given in Pruett and
137 Webb (1993).

138 Muscovite single crystals (12.7 × 12.7 × 0.2 mm³) were purchased from the Asheville-
139 Schoonmaker Mica Company (USA) and milled to a fine powder with an agate ball mill. The grain
140 size fraction < 63 μm of the mineral powder was used for the batch sorption experiments. Its SSA was
141 determined to be 9.9 m²/g (Hellebrandt, 2017).

142 The elemental composition of these minerals is shown in Table S1 (Supplementary Material).

143 For comparison purposes, a U(VI)-doped calcium silicate hydrate (C-S-H) phase with a Ca/Si
144 ratio of 1.2 was synthesized in alkali-free solution according to the procedure described in Wolter et
145 al. (2019b). The equilibration time was 67 d, the final U(VI) loading was 8.3×10⁻⁴ mol/kg at a pH of
146 12.1.

147 Background electrolytes in the sorption experiments were either pure NaCl (p.a., Carl Roth,
148 Karlsruhe, Germany) solutions as well as mixed NaCl/CaCl₂ (puriss. AppliChem, Darmstadt,
149 Germany) or NaCl/SrCl₂ (p.a., Merck, Darmstadt, Germany) solutions. All solutions were prepared
150 with deionized water (18.2 MΩ cm; mod. Milli-RO/Milli-Q-System, Millipore, Schwalbach,
151 Germany) which was additionally degassed prior to solution preparation by boiling for about 2 h to
152 avoid any introduction of CO₂ and O₂ and was purged for several minutes with Ar in case of Np(VI)
153 sorption experiments.

154 Added U(VI) originated from a 1×10⁻³ M stock solution (U_{nat} in 0.005 M HClO₄). The ²³⁷Np(VI)
155 stock solution, where ²³⁷Np was in secular equilibrium with ²³³Pa, was prepared as described in
156 Amayri et al. (2011). The ⁴⁵Ca stock solution was purchased from PerkinElmer (Waltham, USA) as
157 ⁴⁵CaCl₂ in aqueous solution and had a tracer concentration of 2×10⁻¹¹ M.

158 **2.2. Batch sorption experiments**

159 Experiments were performed in glove boxes under carbonate-free, inert gas atmosphere: N₂
160 (U(VI) experiments) or Ar (Np(VI) experiments). The mineral powders were weighed in 15 mL
161 polypropylene centrifuge tubes (Greiner Bio-One, Frickenhausen, Germany) and suspended with
162 10 mL of the respective background electrolyte. The experimental parameters of all batch sorption
163 experiments are compiled in Table 1. All sorption samples were prepared in duplicate.

164 In the experiments with U(VI), suspensions were pre-conditioned with pH-adjustments by diluted
165 NaOH (p.a., Carl Roth) or HCl (p.a., ACS, ISO, Carl Roth) every other day until a constant pH value
166 (± 0.05) was reached (approx. two weeks). The pH was measured with an InoLab pH 7110 pH meter
167 (WTW, Weilheim, Germany) and a SenTix MIC glass electrode (WTW). Three point calibration was
168 executed with WTW buffer solutions (pH 6.865, 9.180 and 12.454; WTW). During pre-equilibration,
169 samples were placed in an end-over-end rotator.

170 In the experiments with Np(VI), pH and E_h values were measured with an inoLab pH/Cond 720
171 meter (WTW), equipped with a temperature sensor WTW TFK 150. The BlueLine 16 pH electrode
172 (Schott Instruments GmbH, Mainz, Germany) was calibrated using certified DIN buffer solutions (see
173 above). The BlueLine 31 Rx redox electrode (Schott Instruments) was checked regularly with a
174 +640 mV redox standard (Schott Instruments). The redox potentials measured against Ag/AgCl were
175 converted to standard hydrogen electrode (SHE) by adding 210 mV to the measured potential.

176 After pre-equilibration, U(VI), Np(VI) or Ca²⁺ were added to the suspensions by pipetting
177 calculated volumes of the respective stock solution. In the experiments with Np(VI), its hexavalent
178 oxidation state was prepared by fuming a ²³⁷Np stock solution several times with 1 M HClO₄, but
179 never to complete dryness. The oxidation state +VI was stabilized by addition of an aliquot of 2 M
180 NaClO to the kaolinite suspensions to yield a hypochlorite concentration of 0.02 M in the batch
181 samples. The concentration and the oxidation state of ²³⁷Np in the stock solution were determined by
182 γ -ray spectroscopy and UV-Vis spectroscopy, respectively. In the Ca sorption experiments, CaCl₂
183 spiked with 1×10^{-12} M ⁴⁵Ca²⁺ was used for the stock solution. Initial RN concentrations in the different
184 experiments are listed in Table 1.

185

186 Table 1: Experimental parameters of the batch sorption experiments.

RN	Experiment	Mineral	Electrolyte	S/L / g/L	[RN] / M	pH
U(VI)	pH edge	Ca-bentonite	0.1 M NaCl	10	5×10^{-7}	8-13
		syn. kaolinite	0.1 M NaCl	0.5	5×10^{-7}	10-13
			0.1 M NaCl + 0.02 M CaCl ₂	0.5	5×10^{-7}	10-13
		muscovite	0.1 M NaCl	3	5×10^{-7}	8-13
			0.1 M NaCl + 0.02 M CaCl ₂	3	5×10^{-7}	8-13
			0.1 M NaCl + 0.02 M SrCl ₂	3	5×10^{-7}	10-13
Np(VI)	pH edge	nat. kaolinite	0.1 M NaCl	3	1×10^{-7}	8-12
			0.1 M NaCl + 0.02 M CaCl ₂	3	1×10^{-7}	8-12
Ca(II)	S/L ratio	Ca-bentonite	-	0.2-20	2×10^{-4}	10
	pH edge	Ca-bentonite	-	10	2×10^{-4}	8-13

187

188 The sorption time was always seven days for U(VI) and three days for Np(VI) based on previous
 189 kinetic sorption experiments (Amayri et al., 2011; Philipp et al., 2019). Sorption time for Ca²⁺ was one
 190 day. During this time, the samples were rotated in an end-over-end shaker. Final pH values were
 191 determined at the end of the sorption experiments.

192 For phase separation, U(VI) and Ca²⁺ sorption samples were centrifuged at 6800×g for 30 min in
 193 an Avanti J-20 XP centrifuge (Beckman Coulter, Fullerton, USA). Np(VI) samples were separated at
 194 4025×g for 60 min in a SIGMA 3K30 centrifuge (Sigma Laborzentrifugen GmbH, Osterode,
 195 Germany).

196 U_{nat} and Ca concentrations in the supernatants were measured by ICP-MS (NexION 350X,
 197 PerkinElmer, Waltham, USA), while equilibrium concentrations of ²³⁷Np after sorption were
 198 determined by ICP-MS (Agilent ICP-MS 7500ce, Agilent Technologies, Santa Clara, CA, USA). ⁴⁵Ca
 199 concentrations in the supernatants were determined by liquid scintillation counting (LSC; Winspectral
 200 α/β , Wallac 1414, PerkinElmer, USA), using an Ultima GoldTM scintillation cocktail (PerkinElmer).

201 From the initial (c_0) and equilibrium (c_{eq}) RN concentrations in solution (M), the percentage of
 202 RN sorption was calculated according to Eq. (1).

$$RN \text{ sorbed} / \% = \frac{c_0 - c_{eq}}{c_0} \times 100\% \quad (1)$$

203 **2.3. Zeta potential measurements**

204 The surface charge of Ca-bentonite particles was determined by zeta potential measurements
205 (Zetasizer Nano ZS, Malvern Instruments, Malvern, United Kingdom). A total of eleven Ca-bentonite
206 suspensions (0.1 g/L) in the pH range 8–13 were prepared in each 0.1 M NaCl, 0.1 M NaCl + 0.02 M
207 CaCl₂ and 0.1 M NaCl + 0.02 M SrCl₂ in order to evaluate the effect of pH, ionic strength and Ca²⁺ or
208 Sr²⁺ concentrations on the surface charge. Results were averaged over ten measurements, each
209 consisting of 10–50 scans.

210 **2.4. Luminescence spectroscopy**

211 Site-selective TRLFS was applied to investigate the U(VI) species sorbed on the surface of
212 Ca-bentonite, muscovite and kaolinite. Samples were prepared under carbonate-free N₂ atmosphere as
213 described in section 2.2 but with lower S/L ratio (0.3 g/L) in order to increase the U(VI) surface
214 coverage. Two samples were prepared with Ca-bentonite in diluted Gipshut solution (2.5 M NaCl,
215 0.02 M CaCl₂, 0.02 M Na₂SO₄, and 0.0051 M KCl; *I* = 2.63 M) at pH 11, where sorption is at
216 maximum: One with the same U(VI) concentration as in the pH-dependent sorption experiments
217 (5×10⁻⁷ M) and one with a U(VI) concentration two orders of magnitude higher than that (5×10⁻⁵ M)
218 to provoke U(VI) precipitation for comparison. Additionally, one sample was prepared with Ca-
219 bentonite in diluted Gipshut solution at pH 12.5.

220 U(VI) sorption on muscovite was investigated in 0.1 M NaCl at pH 11 and in 0.1 M NaCl +
221 0.02 M CaCl₂ at pH 12. Kaolinite samples were prepared in 0.1 M NaCl at pH 10 and in 0.1 M NaCl +
222 0.02 M CaCl₂ at pH 12. To account for potential formation of C-S-H phases in the Ca-containing
223 mineral suspensions and the subsequent association of U(VI) with this secondary phase, also the
224 U(VI) speciation on a synthetic U(VI)-doped C-S-H phase was investigated (Ca/Si = 1.2, U(VI)
225 loading = 8.3×10⁻⁴ mol/kg, pH 12.1).

226 Prior to the spectroscopic measurements, the samples were ultracentrifuged (187,000×*g*), and the
227 wet paste pellets were transferred into copper sample holders with a sealable quartz glass lid. The

228 sorption samples were measured with a pulsed Nd:YAG (Continuum Surelite II, San Jose, USA)
229 pumped dye laser setup (Radiant Dyes Narrow Scan K, Wermelskirchen, Germany). The C-S-H
230 sample was measured with a tunable diode pumped solid state (DPSS) laser (Ekspla, NT230,
231 Vilnius, Lithuania). The emitted luminescence light was directed into a spectrograph (Shamrock
232 303iAndor Oxford Instruments, Abingdon, United Kingdom) equipped with a polychromator with
233 300, 600, and 1200 lines/mm gratings, and the emission was monitored with an intensified CCD
234 camera (Andor iStar, Oxford Instruments) 10 μ s after the exciting laser pulse in a time window of
235 10 ms. The sorption samples were excited in the wavelength range between 460 and 520 nm with a
236 step size of 0.2 nm. During these measurements, the laser pulse energy and the exact excitation
237 wavelength were monitored with an optical power meter (Newport 1918-R, Irvine, USA) and a
238 wavelength meter (High Finesse WS-5, Tübingen, Germany), respectively. U(VI) associated with the
239 C-S-H phase was excited in the wavelength range between 340 and 390 nm due to a lower suppression
240 of the laser signal using the DPSS laser set-up.

241 Additionally, time-resolved luminescence spectra were recorded at selected excitation
242 wavelengths with a temporal step size of 10 μ s. To achieve the desired spectral resolution, the solid
243 samples were cooled to \sim 10 K in a helium-refrigerated cryostat.

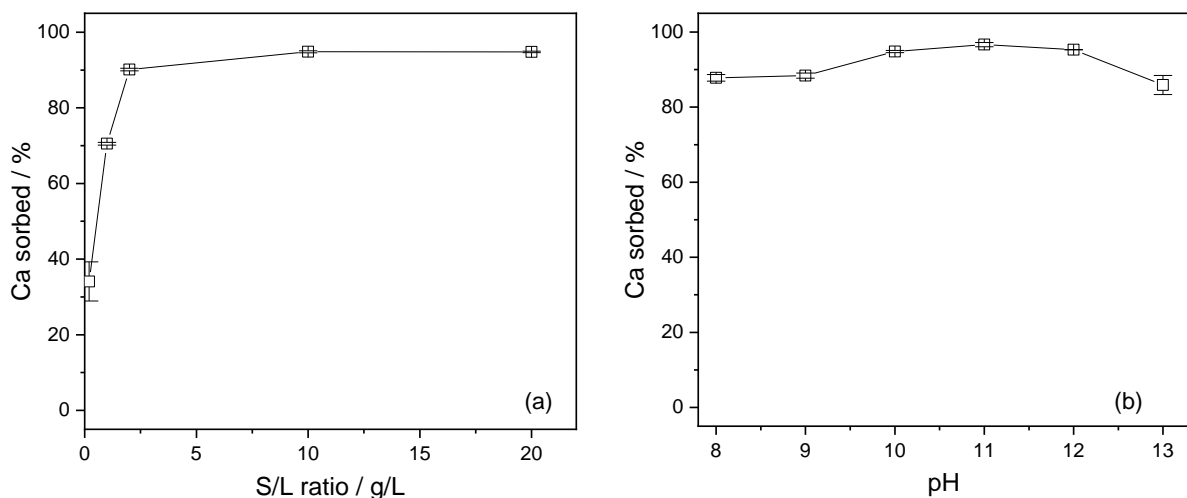
244 **3. Results and discussion**

245 **3.1. Ca(II) and Sr(II) sorption on Ca-bentonite at (hyper)alkaline conditions**

246 The sorption of Ca^{2+} on Ca-bentonite was investigated in batch sorption experiments as a function
247 of S/L ratio and pH value. The initial Ca^{2+} concentration of 2×10^{-4} M was chosen based on estimations
248 for a monolayer saturation of the Ca-bentonite surface with Ca^{2+} cations considering the literature
249 value for the montmorillonite surface site density of 2×10^{-5} mol/g (Wieland et al., 1994).

250 The batch experiments as a function of S/L ratio prove that Ca^{2+} strongly adsorbs to the
251 Ca-bentonite surface, when enough solid is present (i.e., sufficient sorption sites are available)
252 (Fig. 1a), reaching a plateau of $> 90\%$ sorption at S/L ratios above 2 g/L. Based on these results, a S/L
253 ratio of 10 g/L was chosen for the pH-dependent sorption experiments, in order to provide enough
254 sites for unrestricted Ca^{2+} adsorption. As shown in Fig. 1b, sorption of Ca^{2+} was very high in the whole

255 investigated pH range 8–13. Sorption increases with increasing pH from 88% at pH 8 to a maximum
 256 of 97% at pH 11. The slight decrease to 86% sorption at pH 13 is attributed to a beginning dissolution
 257 of minerals within the bentonite, as observed in leaching experiments in Philipp et al. (2019). Strong
 258 retention of Ca^{2+} and its chemical analogue Sr^{2+} has already been observed on bentonite (Cherian et
 259 al., 2018; He et al., 2016; Missana and García-Gutiérrez, 2007; Missana et al., 2008), montmorillonite
 260 (Sugiura et al., 2021), muscovite (Fenter et al., 2007; Schlegel et al., 2006), kaolinite (Chen et al.,
 261 2014), illite (Fuller et al., 2016), silica and alumina (Szymanek et al., 2021). At $\text{pH} < 8$, the
 262 predominant retention mechanism is cation exchange, which is largely independent of pH, but highly
 263 sensitive to ionic strength (Missana and García-Gutiérrez, 2007). At $\text{pH} > 8$, also surface complexation
 264 contributes to the retention of Ca^{2+} . Missana and García-Gutiérrez (2007), Sugiura et al. (2021) and
 265 Szymanek et al. (2021) were only able to model an observed increase in Ca^{2+} sorption at $\text{pH} > 8$ by the
 266 introduction of surface complexes on the amphoteric edge sites of the minerals.



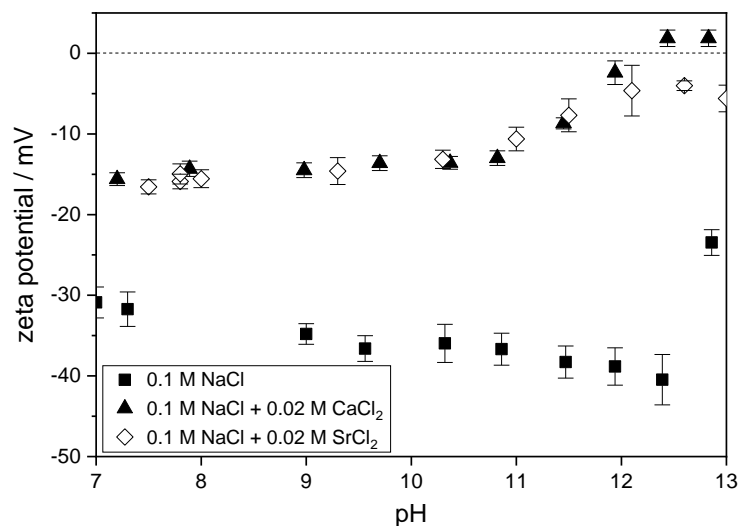
267

268 Figure 1: Sorption of calcium (2×10^{-4} M spiked with 1×10^{-12} M ^{45}Ca) on Ca-bentonite as a function of
 269 S/L ratio (pH 10) (a) and as a function of pH (S/L = 10 g/L) (b). The corresponding K_d -based graphs
 270 are shown in Fig. S1 (Supplementary Material).

271 An increase of the pH value leads to a successive deprotonation of the clay mineral surface
 272 ($\text{SOH} \leftrightarrow \text{SO}^- + \text{H}^+$), promoting surface complexation. Accordingly, Schlegel et al. (2006) and Fenter
 273 et al. (2007) also observed a contribution of surface complexation to Ca^{2+} and Sr^{2+} adsorption on the
 274 mica (001) surface, expressed in the partial removal of the hydration shell. Consequently, surface

275 complexation is assumed to contribute significantly to the strong Ca^{2+} retention on Ca-bentonite at pH
276 8–13 observed in the present study.

277 The adsorption of Ca^{2+} on the Ca-bentonite surface is additionally evidenced by the measurement
278 of the zeta potential of Ca-bentonite with added CaCl_2 . Compared to the measurement in pure 0.1 M
279 NaCl, the addition of 0.02 M Ca^{2+} leads to a much less negative surface charge over the entire
280 investigated pH range 7–13 (Fig. 2). Part of the difference can be explained by the exchange of Ca^{2+}
281 by Na^+ in the Ca-bentonite upon suspension in NaCl, commonly evoking more negative surface
282 charge. However, the fact that the zeta potential does not become more negative with increasing pH in
283 the presence of Ca^{2+} and strongly increases at $\text{pH} > 10$ proofs additional surface complexation of Ca^{2+} .
284 The presence of Ca^{2+} does not result in a complete reversal of surface charge, however, negative
285 surface charge is partly compensated. As the average charge of all existing surface sites is measured
286 with this bulk technique, a partial compensation of negative surface charge implies the existence of
287 locally positively charged sites due to surface complexation of Ca^{2+} . Beside the effect of Ca^{2+} , also the
288 influence of Sr^{2+} on the surface charge was investigated. In 0.1 M NaCl + 0.02 M SrCl_2 , the effect on
289 the surface charge is almost identical to the experiment with Ca^{2+} (Fig. 2). Both divalent cations, Ca^{2+}
290 and Sr^{2+} , having the same charge compensating effect, indicate that the charge of the cation is the main
291 driving factor for the observed changes in the zeta potential.



292

293 Figure 2: Surface potential of Ca-bentonite (0.1 g/L) as a function of pH value and background
294 electrolyte.

295 Similar impact on surface charge due to adsorption of Ca^{2+} at alkaline conditions has been
296 previously reported for different types of bentonite (Cherian et al., 2018; Ho and Handy, 1963),
297 kaolinite (Atesok et al., 1988; Farooq et al., 2011), alumina and silica (Szymanek et al., 2021) and
298 cementitious material (Pointeau et al., 2006; Viallis-Terrisse et al., 2001). In some of these studies
299 even a reversal of charge was observed.

300 Both batch sorption experiments with Ca^{2+} and zeta potential measurements have shown that Ca^{2+}
301 strongly adsorbs to the Ca-bentonite surface and consequently, generates alternative sorption sites for
302 anionic actinyl hydroxides. The resulting Ca-induced changes in U(VI) and Np(VI) sorption are
303 presented in section 3.2.

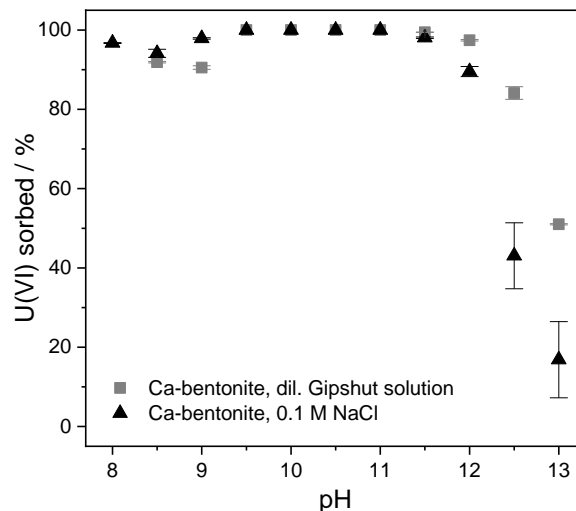
304 **3.2. Effect of Ca(II) and Sr(II) on U(VI) and Np(VI) sorption on Ca-bentonite, kaolinite and** 305 **muscovite**

306 As the previous U(VI) sorption experiments on Ca-bentonite in diluted Gipshut solution were
307 conducted in the presence of Ca^{2+} (Philipp et al., 2019), the aim was to perform similar experiments,
308 but with the exclusion of Ca^{2+} . For that purpose, mineral suspensions were prepared in NaCl
309 background solutions instead of the diluted Gipshut solution. Moreover, in addition to Ca-bentonite,
310 the mineral phases kaolinite and muscovite, which do not contain intrinsic Ca that could be leached
311 during the experiment but serve as analogues for montmorillonite/bentonite, were chosen for further
312 batch sorption experiments. Assuming that Ca^{2+} is responsible for enabling sorption of actinyl
313 hydroxide complexes, U(VI) and Np(VI) retention is expected to be radically decreased in these
314 experiments between pH 10 and 12 compared to their retention in the presence of Ca^{2+} .

315 **3.2.1. U(VI) sorption on Ca-bentonite**

316 The batch sorption experiments in our previous study (Philipp et al., 2019) have shown a very
317 high U(VI) retention on Ca-bentonite in diluted Gipshut solution up to pH 12. Only at $\text{pH} > 12$,
318 sorption decreased to approx. 50% at pH 13. The concentrations of Ca^{2+} in these samples were very
319 high due to the composition of the diluted Gipshut solution (2.5 M NaCl, 0.02 M CaCl_2 , 0.02 M
320 Na_2SO_4 , and 0.0051 M KCl). In the present study, the experiment was repeated in only 0.1 M NaCl
321 background electrolyte. The obtained results are very similar to the experiment with diluted Gipshut

322 solution (Fig. 3). Apart from a slight decline of the U(VI) uptake at a pH around 9, likely due to a
 323 minor intrinsic carbonate impurity in the Ca-bentonite material, a very high U(VI) retention up to pH
 324 12 can be seen. Uranyl carbonate species have been shown to reduce U(VI) sorption in previous
 325 studies (Meleshyn et al., 2009; Stockmann et al., 2022), however, as the pH increases, the role of
 326 carbonates decreases as U(VI) hydroxo complexes become prevailing. The decrease in sorption above
 327 pH 12 is slightly more pronounced in the experiment with 0.1 M NaCl (Fig. 3). However, the
 328 postulated drop of U(VI) retention at pH > 10 due to the absence of Ca could not be observed. In fact,
 329 still considerably high Ca concentrations, leached from Ca-bentonite, were detected in the
 330 supernatants (e.g., 9.8×10^{-4} M at pH 11). Previous leaching tests with the Ca-bentonite revealed that
 331 Ca is released from the mineral phase into the solution under the given conditions (Philipp et al.,
 332 2019). That means that Ca-free sorption samples with a potentially different U(VI) sorption behavior
 333 can only be obtained with other mineral phases which do not contain any Ca that could potentially be
 334 leached.



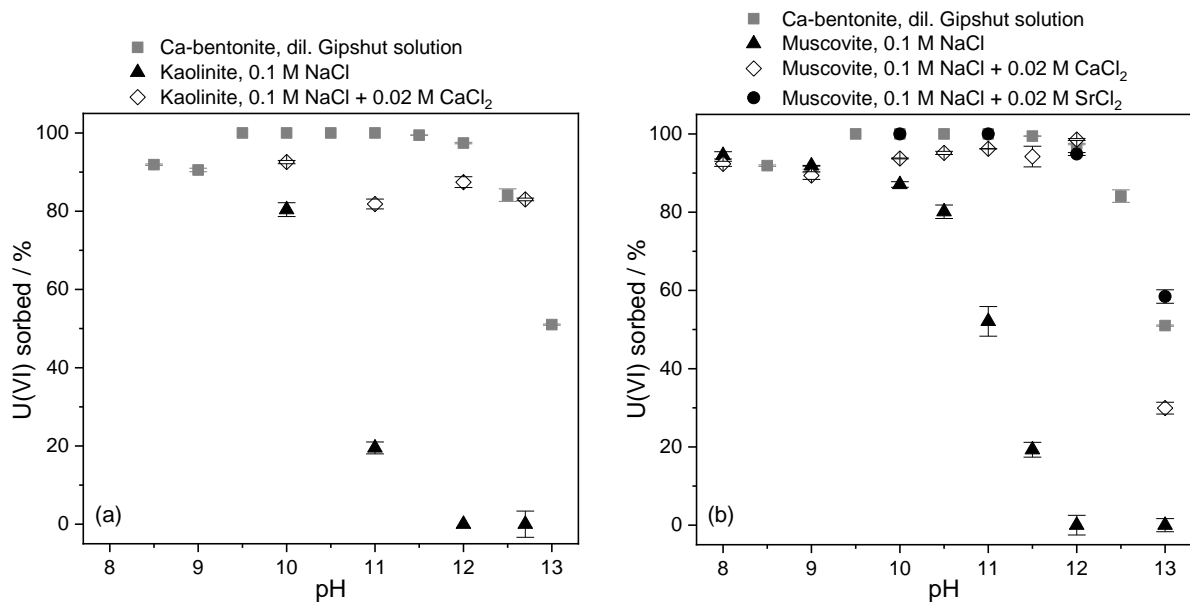
335
 336 Figure 3: U(VI) sorption ($[U(VI)] = 5 \times 10^{-7}$ M) on Ca-bentonite (10 g/L) in 0.1 M NaCl as a function
 337 of pH. The U(VI) sorption on Ca-bentonite ($[U(VI)] = 5 \times 10^{-7}$ M, 10 g/L) in diluted Gipshut solution is
 338 shown for comparison (Philipp et al., 2019). The corresponding K_d -based graphs are shown in Fig. S2.

339 3.2.2. U(VI) sorption on synthetic kaolinite

340 Experiments were performed at pH 10, 11, 12 and 12.7 both in 0.1 M NaCl and 0.1 M NaCl +
 341 0.02 M $CaCl_2$ (Fig. 4a). In contrast to the experiments with Ca-bentonite, the sorption of U(VI) on
 342 synthetic kaolinite is decreasing dramatically at $pH \geq 10$ in the absence of Ca^{2+} . At pH 12, sorption

343 reaches 0%, supporting the hypothesis that high U(VI) retention at pH 10–12 cannot be sustained in
 344 the absence of Ca^{2+} . Measured Ca^{2+} concentrations in the supernatant after the sorption experiment
 345 were as low as 4×10^{-6} M. This seems to be sufficiently low to prevent U(VI) sorption to the mineral
 346 surface at hyperalkaline conditions. The origin of trace amounts of Ca^{2+} in the supernatant could be
 347 contamination of laboratory equipment such as the pH electrode, or impurity of the NaCl electrolyte.

348 Experiments with added CaCl_2 were performed in order to verify that the decreased U(VI)
 349 retention at $\text{pH} \geq 10$ is really associated to the lower Ca^{2+} concentration and not to the different
 350 mineral structure of kaolinite compared to Ca-bentonite. In 0.1 M NaCl + 0.02 M CaCl_2 , U(VI)
 351 sorption on kaolinite is very high ($> 80\%$) up to pH 12.7 (Fig. 4a). Therefore, it can be unequivocally
 352 concluded that the presence of Ca significantly enhances U(VI) retention between pH 10 and 13.



353
 354 Figure 4: U(VI) sorption ($[\text{U(VI)}] = 5 \times 10^{-7}$ M) on synthetic kaolinite (0.5 g/L) (a) and muscovite
 355 (3 g/L) (b) in 0.1 M NaCl, 0.1 M NaCl + 0.02 M CaCl_2 and 0.1 M NaCl + 0.02 M SrCl_2 as a function
 356 of pH. The U(VI) sorption on Ca-bentonite ($[\text{U(VI)}] = 5 \times 10^{-7}$ M, 10 g/L) in diluted Gipschut solution is
 357 shown for comparison (Philipp et al., 2019).

358 3.2.3. U(VI) sorption on muscovite

359 The U(VI) sorption on muscovite is comparable to that of kaolinite (Fig. 4b). In 0.1 M NaCl,
 360 U(VI) sorption decreases first slowly at $\text{pH} > 8$ and then rapidly at $\text{pH} \geq 10$, reaching 0% at pH 12.
 361 Measured Ca^{2+} concentrations in the supernatant after the sorption experiment were about 6.3×10^{-6} M,
 362 apparently low enough to not trigger substantial U(VI) retention.

363 The experiments with addition of CaCl_2 exhibit a high U(VI) sorption up to pH 12 and follow a
364 similar trend as sorption experiments with Ca-bentonite (Fig. 4b). Thus, as already concluded for
365 synthetic kaolinite, the low retention at $\text{pH} \geq 10$ in 0.1 M NaCl is not a consequence of the different
366 mineral structure but is directly related to the absence of Ca^{2+} .

367 A complementary pH-dependent U(VI) sorption experiment was conducted in 0.1 M NaCl +
368 0.02 M SrCl_2 in order to investigate if the presence of Sr^{2+} can have the same positive effect on U(VI)
369 retention as Ca. As shown in Fig. 4b, in the presence of Sr^{2+} indeed an almost identical U(VI) sorption
370 behavior was observed, with very high U(VI) retention up to pH 12. This suggests that the effect of
371 enabling U(VI) adsorption is not attributed to exclusive properties of Ca^{2+} but to the charge of bivalent
372 cations in general. The underlying retention mechanisms are further discussed in section 3.4.

373 **3.2.4. Np(VI) sorption on kaolinite KGa-1b**

374 The sorption of Np(VI) on natural kaolinite (KGa-1b) was studied in the pH range 8–12 using
375 two different electrolytes, i.e., 0.1 M NaCl without and with addition of 0.02 M CaCl_2 (Fig. 5). To
376 ensure the stability of the +VI oxidation state of Np, strongly oxidizing conditions were provided by
377 the addition of 0.02 M NaClO. As can be seen from the Pourbaix diagram (Fig. S3), the measured E_h
378 values indicate the dominance of Np(VI) in the pH range studied.

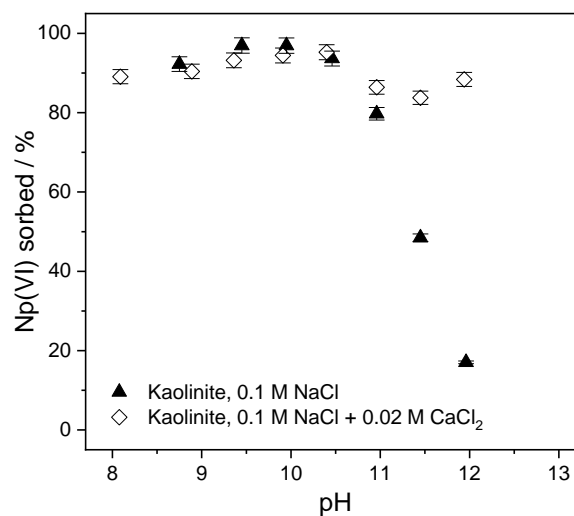
379 The sorption of Np(VI) on kaolinite in the pH range 8.0–10.5 is between 89–97% and
380 independent of the presence of Ca^{2+} (Fig. 5). Above pH 11.0, Np(VI) sorption decreases strongly in
381 the absence of Ca^{2+} , from 79% to 17% at pH 12. In the experiments with 0.02 M CaCl_2 in the
382 background electrolyte, sorption remains above 80% in the pH range 11.0–11.5, reaching 90% at pH
383 12. The shallow minimum in the sorption curve between pH 11 and 12 in the presence of Ca^{2+} can be
384 explained by two competing effects, i.e., decreasing sorption in 0.1 M NaCl and increasing Np(VI)
385 retention under the influence of Ca^{2+} . A similar shallow minimum can be seen in the sorption data of
386 U(VI) on synthetic kaolinite (Fig. 4a).

387 The precipitation of Ca neptunates in this pH range can be excluded under the experimental
388 conditions. Fellhauer et al. (2018) studied the solubility of $\text{Ca}_x\text{NpO}_{3-x}(\text{hyd},\text{s})$ in alkaline CaCl_2
389 solutions. For example, the Np(VI) equilibrium concentration in 0.25 M CaCl_2 in the pH range 8.8–

390 12.0 was equal to approximately 5×10^{-7} M Np(VI) (see Fig. 6a in Fellhauer et al. (2018)). The
391 equilibrium concentration in the present batch experiment with 0.1 M NaCl + 0.02 M CaCl₂ at pH 12.0
392 was about one order of magnitude lower, i.e., approximately 1×10^{-8} M Np(VI).

393 The decrease of Np(VI) sorption at pH > 10 in the Ca-free background electrolyte is not as
394 pronounced as observed for the U(VI) sorption on synthetic kaolinite (Fig. 4a). This can be explained
395 by the fact that, in contrast to the synthetic kaolinite, the natural kaolinite contains small amounts of
396 Ca (see Table S1) that can be leached during the sorption experiment.

397 Nonetheless, the sorption experiments with Np(VI) confirm the strong influence of Ca²⁺ on the
398 retention of hexavalent actinides on kaolinite in the hyperalkaline pH range. Due to the similar
399 chemistry and aqueous speciation of Np(VI) and U(VI) (Fig. S4), underlying retention mechanisms
400 are expected to be equivalent. These are elucidated with the help of U(VI) luminescence spectroscopy
401 in the following section.



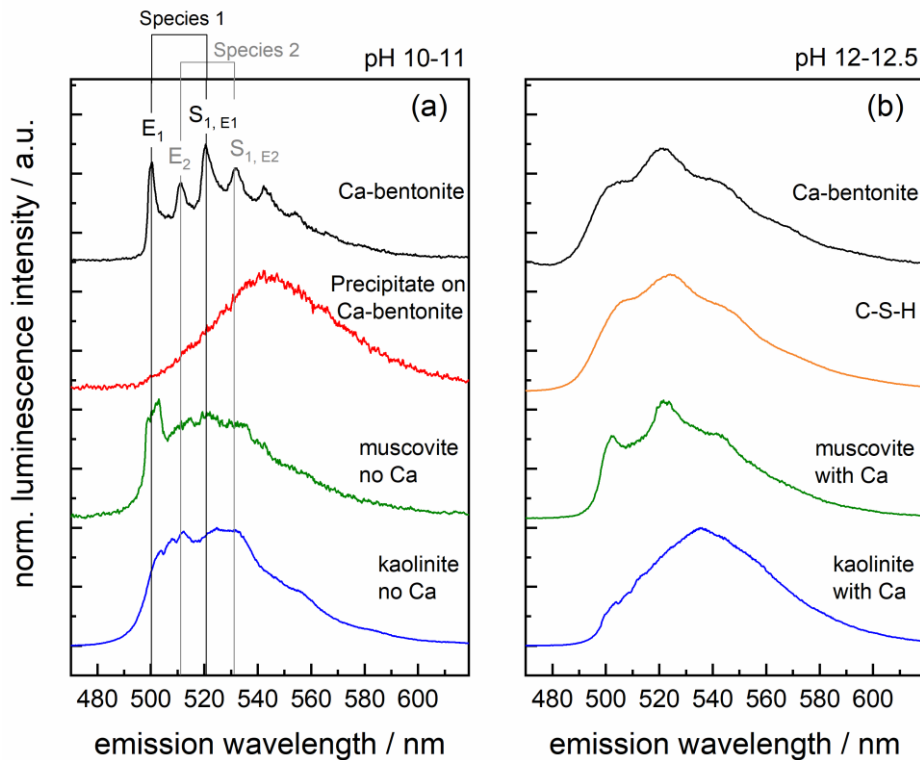
402

403 Figure 5: Np(VI) sorption ($[Np(VI)] = 1 \times 10^{-7}$ M) on kaolinite KGa-1b (3 g/L) in 0.1 M NaCl and
404 0.1 M NaCl + 0.02 M CaCl₂ as a function of pH under oxidizing conditions (0.02 M NaClO) and Ar
405 atmosphere.

406 3.3. Site-selective TRLFS of Ca-induced U(VI) surface complexes

407 The site-selective TRLFS investigations of U(VI) sorption on the various aluminosilicate minerals
408 were conducted in two pH regimes: at pH 10 (kaolinite) or 11 (Ca-bentonite, muscovite), where the
409 effect of Ca²⁺ on U(VI) sorption on the solid phases is small or negligible, and at pH 12–12.5, where
410 Ca²⁺ has a strong effect on U(VI) retention. In case of muscovite and kaolinite, the sorption

411 experiments were performed in the absence (pH 10–11) and presence of 0.02 M Ca (pH 12–12.5),
 412 whereas diluted Gipshut solution was applied as background electrolyte in case of Ca-bentonite
 413 experiments. From the recorded emission spectra presented in Fig. 6, a different U(VI) speciation in
 414 the mineral suspensions at the two different solution conditions is apparent. A direct comparison of the
 415 recorded emission spectra of the aluminosilicate samples in the two different pH-regimes can be found
 416 in Fig. S5.



417

418 Figure 6: U(VI) emission spectra obtained from wet paste aluminosilicate samples at pH 10–11 (a) and
 419 at pH 12–12.5 (b). The excitation wavelength used to obtain the emission spectrum and the pH value
 420 of the sample suspension were (a) kaolinite ($\lambda_{\text{ex}} = 499.7$ nm, pH 10), muscovite ($\lambda_{\text{ex}} = 499.7$ nm,
 421 pH 11), Ca-bentonite, sorbate and precipitate ($\lambda_{\text{ex}} = 499.7$ nm, pH 11) and (b) kaolinite ($\lambda_{\text{ex}} =$
 422 499.7 nm, pH 12), muscovite ($\lambda_{\text{ex}} = 499.7$ nm, pH 12), Ca-bentonite ($\lambda_{\text{ex}} = 496.7$ nm, pH 12.5), C-S-H
 423 ($\lambda_{\text{ex}} = 342.0$ nm, pH 12.1; Ca/Si = 1.2). The U(VI) loading of Ca-bentonite, muscovite and kaolinite
 424 was 1.67×10^{-3} mol/kg, that of the C-S-H phase was 8.3×10^{-4} mol/kg and that of the ‘precipitate on Ca-
 425 bentonite’ was 1.7×10^{-1} mol/kg.

426 As described previously (Philipp et al., 2019), the emission spectrum of the Ca-bentonite sample
 427 at pH 11 (top, black spectrum) shows pronounced luminescence line-narrowing as a result of resonant
 428 excitation of single U(VI) species in the sample, using an excitation wavelength of 499.7 nm. For this
 429 sample as well as for the other aluminosilicate ones, a low total U(VI) concentration of 5×10^{-7} M was
 430 used, corresponding to a U(VI) loading of 1.67×10^{-3} mol/kg, to suppress U(VI) (surface) precipitation.

431 For the sample ‘precipitate on Ca-bentonite’ with 5×10^{-5} M U(VI) (loading 1.7×10^{-1} mol/kg),
432 however, a broad spectrum (red trace) is obtained, indicative of surface precipitation as a result of the
433 much higher U(VI) concentration.

434 From the emission spectrum of Ca-bentonite with 5×10^{-7} M U(VI) at pH 11, two U(VI) species
435 could be identified (Philipp et al., 2019). Species 1 is characterized by a resonant electronic transition
436 line (E_1), followed by the lines of vibronic progression on E_1 ($S_{N,E1}$, only $S_{1,E1}$ is indicated in the figure)
437 caused by the vibronic degeneracy of the electronic ground state. The same is true for species 2,
438 however, here a non-resonant excitation takes place. The electronic transition line and the first
439 vibronic progression line are indicated in the figure with E_2 and $S_{1,E2}$, respectively. The calculated
440 stretch vibration frequencies (ν_s), obtained from the spacing between the first two peaks of each
441 species (i.e., between E_1 and $S_{1,E1}$ and between E_2 and $S_{1,E2}$, respectively) are 781 ± 5 cm^{-1} for species
442 1 and 758 ± 12 cm^{-1} for species 2. Based on the lower stretch vibration frequency of species 2,
443 implying a stronger coordination in the equatorial plane by coordinating ligands, this species has been
444 assigned to an inner-sphere sorbed U(VI) complex. Species 1, on the other hand, was assigned to a
445 U(VI) complex with outer-sphere character, based on additional X-ray absorption spectroscopic
446 investigations. More specifically, the EXAFS data showed the presence of a surface complex with a
447 structure resembling that of the $\text{UO}_2(\text{OH})_4^{2-}$ aqueous species and no backscattering signal from surface
448 Al/Si atoms. In the light of the results obtained in our batch sorption experiments, and the adsorption
449 of Ca^{2+} on the bentonite surface, it is very likely that the sorption of the uranyl species is mediated by
450 Ca^{2+} . Thus, the term Ca-mediated complex (species 1) will be used in the following text to describe
451 this U(VI) species.

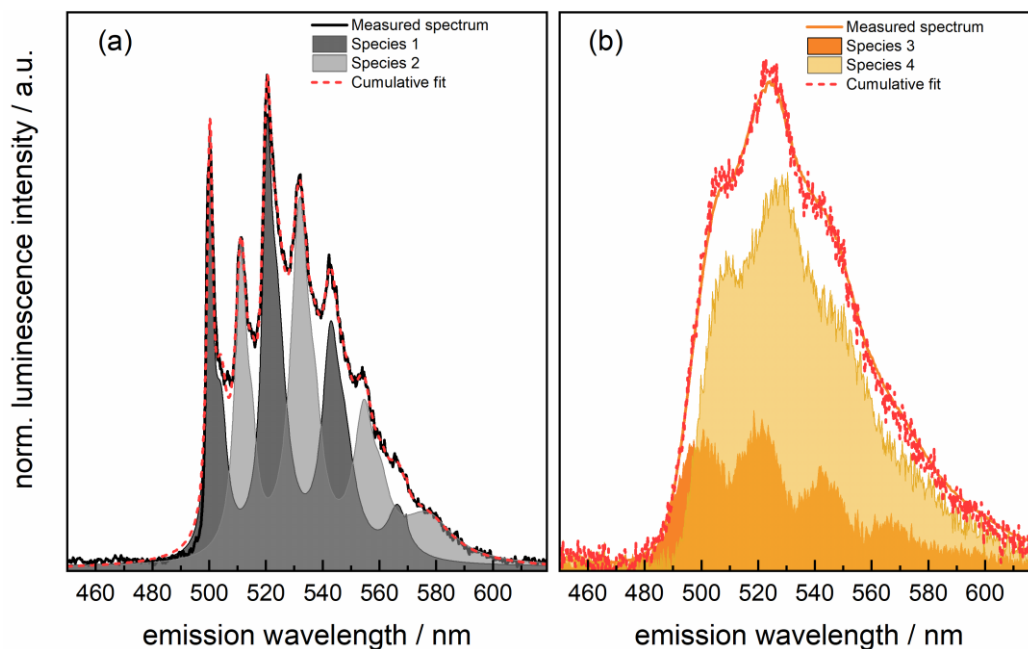
452 In comparison to the Ca-bentonite sample, the line-narrowing of muscovite and kaolinite at pH
453 10–11 (absence of added Ca^{2+}), is much less pronounced at the same excitation wavelength of
454 499.7 nm, Fig. 6a. Such inhomogeneous line broadening following selective excitation has previously
455 been observed for U(VI) sorbed on TiO_2 by Tits et al. (2015). In the same study, the authors
456 investigated U(VI) association with C-S-H phases, for which clear line-narrowing could be observed.
457 As both the set-up for the spectroscopic studies as well as the aqueous chemistry and the total UO_2^{2+}
458 concentration in the samples were identical for both TiO_2 and C-S-H, no apparent reason for the less

459 pronounced luminescence line-narrowing for U(VI) sorption on TiO₂ could be given. Combining the
460 results obtained in the present study and those by Tits et al. (2015), only the spectra of U(VI) sorption
461 experiments with Ca-bentonite and C-S-H phases show pronounced line-narrowing, while the spectra
462 of U(VI) sorption samples with TiO₂, muscovite, and kaolinite do not. Common for Ca-bentonite and
463 C-S-H phases is a swellable structure with an interlayer space that can accommodate water molecules
464 and various counter ions for charge compensation. U(VI) has been shown to sorb in this interlayer
465 space (Kowal-Fouchard et al., 2004; Kremleva et al., 2020; Olivelli et al., 2013). The other minerals,
466 for which the pronounced line-narrowing could not be observed, do not feature such an accessible
467 interlayer space. In muscovite, the interlayer is occupied by potassium cations, while in kaolinite the
468 octahedral and tetrahedral sheets are held together with hydrogen bonds, without any interlayer
469 cations. Thus, in muscovite and kaolinite U(VI) sorption is restricted to the edge sites, significantly
470 reducing the reactive surface area in comparison to Ca-bentonite and C-S-H phases. The reduced
471 reactive surface area causes the distance between the adjacent uranium species to approach the critical
472 Förster distance (Hink et al., 2003), leading to homo-resonance energy transfer. Knowing the U(VI)
473 loading of 1.67×10^{-3} mol/kg and the specific surface area of the minerals, it can be calculated that
474 approx. 1.3, 10.1 and 4.5 uranium atoms are adsorbed on a 10 nm² surface area of Ca-bentonite,
475 muscovite and kaolinite, respectively. Assuming that the sorbed atoms are homogeneously distributed
476 at the surface, the distance between the single adsorbed U(VI) complexes is approx. 2.76 nm on Ca-
477 bentonite, 0.99 nm on muscovite and 1.49 nm on kaolinite. Hence, the distance between the U atoms
478 on muscovite and kaolinite is much closer to the critical Förster distance of 0.7 nm, calculated by Tits
479 et al. (2015), compared to Ca-bentonite, where line-narrowing could be observed.

480 At pH 12 and in the presence of added Ca²⁺, all recorded emission spectra, independent of the
481 excitation wavelength, are broader than at pH 10–11, and for kaolinite a clear red-shift to higher
482 wavelengths has occurred (Fig. 6b). This shift could be due to precipitation from oversaturated
483 solutions, similarly to what was observed for the higher U(VI) concentration in contact with Ca-
484 bentonite (sample ‘precipitate on Ca-bentonite’). For a direct comparison of these emission spectra,
485 the reader is referred to Fig. S6. The spectra are discussed in more detail below, but this result
486 corroborates the role of the interlayer space for additional uranium uptake, which is not available in

487 the case of kaolinite, thus leading to surface saturation and precipitation of non-sorbed uranium from
488 solution.

489 To get a better insight into the U(VI) speciation of the aluminosilicate phases, a decomposition of
490 the measured U(VI) emission spectra of the Ca-bentonite suspension at pH 11 and of the C-S-H phase
491 with a Ca/Si ratio of 1.2 (pH 12.1) was performed to extract spectra of single species. The well-
492 resolved emission spectrum of U(VI) sorption on Ca-bentonite at pH 11 in diluted Gipsbut solution
493 can be described with two single components, denoted species 1 and species 2 (Fig. 7a). From the
494 U(VI)-doped C-S-H phase, two species (species 3 and species 4) with clearly broader emission bands
495 were obtained, Fig. 7b.



496
497 Figure 7: Extracted pure components from the decomposition of the measured U(VI) emission spectra
498 in the Ca-bentonite suspension at pH 11 (a) and the C-S-H phase (Ca/Si = 1.2) at pH 12.1 (b).

499 Interestingly, the emission peak positions of species 1 and species 3 in the Ca-bentonite and the
500 C-H-S sample, respectively, are very similar, pointing towards a similar U(VI) species in these
501 systems (Fig. S7). The calculated stretch vibration frequency of this C-S-H species is 799 cm^{-1} , i.e.,
502 slightly higher than the ν_s for species 1 on Ca-bentonite (781 cm^{-1}). The second species in the C-S-H
503 sample is slightly more red-shifted and has a stretch vibration frequency of 771 cm^{-1} .

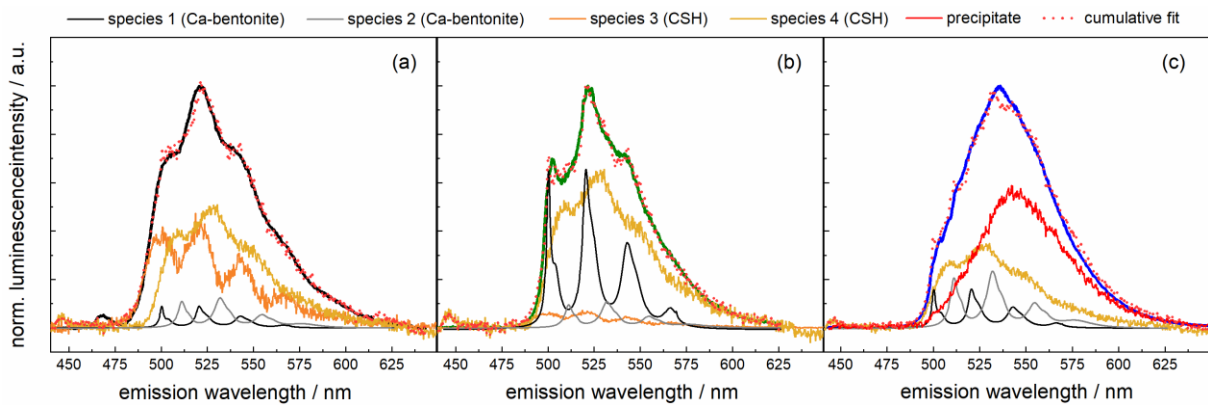
504 In previous studies investigating U(VI) uptake by C-S-H phases with varying Ca/Si ratios, three
505 types of U(VI) species were identified: (i) a surface complex, (ii) a species absorbed in the interlayer

506 region of C-S-H, sometimes referred to in the literature as an incorporated species and (iii) a
507 precipitate, which is observed at increased U(VI) concentration (Tits et al., 2011; Tits et al., 2015;
508 Wolter et al., 2019b). In C-S-H with Ca/Si 0.75-1.65 (Tits et al., 2011), the adsorbed species was
509 characterized by an electronic transition line at $20,150 \pm 60 \text{ cm}^{-1}$ (496 nm) and ν_s ranging between 741
510 and 799 cm^{-1} . The interlayer sorbed species was clearly more red-shifted with $E_1 = 19,824 \pm 52 \text{ cm}^{-1}$
511 (504 nm) and $\nu_s = 742\text{--}769 \text{ cm}^{-1}$. Its proportion was found to increase with time. By Tits et al. (2015),
512 a C-S-H phase with a Ca/Si ratio of 1.07 was investigated with site-selective luminescence
513 spectroscopy. As already mentioned, the samples showed pronounced line-narrowing allowing for a
514 very precise determination of the stretch vibration frequencies of the two identified U(VI) species
515 associated with the solid phase. The first species, which was assigned to an inner-sphere sorbed U(VI)
516 species on the C-S-H surface yielded a ν_s of $758 \pm 10 \text{ cm}^{-1}$. The second species, incorporated in the C-
517 S-H structure, had a lower stretch vibration frequency of $744 \pm 10 \text{ cm}^{-1}$. Thus, both species from Tits
518 et al. (2015) have ν_s values which are lower than those of the species identified in the present study.
519 However, the stretch vibration frequencies were found to increase with increasing excitation energy
520 (ν_{ex}) (see Fig. 5 in Tits et al. (2015)), i.e., with decreasing excitation wavelengths (λ_{ex}). Thus, the
521 differences in stretch vibration frequencies could be explained by the different excitation wavelengths
522 applied in the respective studies: 476–530 nm for C-S-H (Tits et al., 2015), 499.7 nm for Ca-bentonite
523 and 342 nm for C-S-H in the present investigation. Alternatively, a slightly different aqueous U(VI)
524 speciation, arising from the different Ca/Si ratios and subsequently different equilibrium pH values in
525 the study by Tits et al. (2015) and the current one, results in a slightly different U(VI) speciation on/in
526 the C-S-H phase. At pH 12.1 (the equilibrium pH value of the C-S-H suspension in this study), the
527 U(VI) speciation is dominated by the $\text{UO}_2(\text{OH})_4^{2-}$ hydrolysis complex, while the $\text{UO}_2(\text{OH})_3^-$ species is
528 prevailing at slightly lower pH ($10 < \text{pH} < 12$).

529 Since species 3 in the C-S-H sample has a comparatively high stretch vibration frequency,
530 indicating weaker binding in the equatorial plane by the surrounding ligands, and since the emission
531 peak positions agree very well with those of species 1 found in our Ca-bentonite sample, we
532 tentatively assign species 3 in the C-S-H sample to a Ca-mediated sorption complex on the C-S-H

533 surface. Species 4 in the C-S-H sample, on the other hand, is assumed to be absorbed in the C-S-H
534 interlayer space, in agreement with previous studies.

535 To describe the measured spectra of the aluminosilicate minerals obtained in the presence of
536 0.02 M Ca^{2+} at $\text{pH} \geq 12$, the pure component spectra extracted from the Ca-bentonite and C-S-H
537 samples (Fig. 7) as well as the spectrum of the surface precipitate on Ca-bentonite (as a pure
538 component, without further spectral analysis) were used. Figure 8 shows that the composite emission
539 spectra of the three different aluminosilicates can be reproduced with the help of all four extracted
540 emission spectra (species 1 and 2 on Ca-bentonite and species 3 and 4 on C-S-H) as well as the
541 spectrum of the surface precipitate on Ca-bentonite.



542
543 Figure 8: Results of spectral decomposition of the measured U(VI) emission spectra of Ca-bentonite,
544 pH 12.5 (a), muscovite, pH 12 (b) and kaolinite, pH 12 (c) in the presence of 0.02 M CaCl_2 .

545 In all cases, a very minor amount of the inner-sphere sorbed surface complex (species 2,
546 Ca-bentonite) is present. In the kaolinite sample, the majority of the U(VI) signal stems from a surface
547 precipitate, as already assumed based on the pronounced red-shift of this spectrum. In the muscovite
548 and Ca-bentonite samples at pH 12, the Ca-mediated surface complex (species 1, Ca-bentonite) and
549 both sorption complexes in the C-S-H sample (species 3 and 4) are required to explain the data. In
550 both mineral suspensions, the major species is C-S-H species 4, closely followed by the Ca-mediated
551 Ca-bentonite and C-S-H complexes (species 1 and 3, respectively). Note, exact percentages of the
552 present species cannot be given due to the different excitation wavelengths used in the present study
553 and the different luminescence quantum yields of the species. These results, however, clearly indicate
554 that C-S-H phases are formed in all mineral suspensions when Ca is present in the system, and
555 consequently, the U(VI) speciation is a mixture of Ca-mediated surface complexes on either the

556 aluminosilicate mineral and/or the newly formed C-S-H phase (species 1 or 3), and species absorbed in
557 the C-S-H interlayer space (species 4). A detailed discussion of the underlying retention mechanisms,
558 combining the results of the batch sorption experiments and luminescence spectroscopy, follows in
559 section 3.4.

560 **3.4. Discussion of underlying retention mechanisms**

561 The batch sorption experiments with Ca-bentonite, synthetic and natural kaolinite, and muscovite
562 in different background electrolytes demonstrate that certain amounts of dissolved Ca^{2+} enable U(VI)
563 and Np(VI) retention at pH 10–13 despite the anionic character of prevailing aqueous species.

564 The TRLFS results reveal that the underlying U(VI) retention mechanisms are (i) sorption onto
565 the aluminosilicate minerals, apparently facilitated by a bridging effect of Ca between the anionic
566 actinide complexes and the negatively charged mineral surfaces (Ca-mediated sorption), and (ii) inner-
567 sphere sorption in the interlayer region of C-S-H phases, which most likely form as secondary mineral
568 phases in the presence of Ca^{2+} . The inner-sphere sorption of U(VI) onto the primary aluminosilicate
569 minerals plays only a minor role at hyperalkaline conditions. The retention mechanisms are discussed
570 below.

571 The proposed mechanism of Ca-bridging uranyl sorption is similar to so called type B ternary
572 surface complexation (Bradl, 2005; Hubbard, 2002). Such ternary type B surface complexes form by
573 coordination of a metal to a sorbed ligand, thus have the configuration surface \equiv ligand – metal. In
574 contrast to type B surface complexes, in the present study the metal (U(VI) or Np(VI)) is not only
575 bridged via the ligand (OH) but also via an additional metal cation (Ca^{2+} or Sr^{2+}) (surface \equiv $\text{Ca}^{2+}/\text{Sr}^{2+}$ –
576 ligand – metal). Such complex systems, exceeding simple coordination of a metal to the surface or
577 ternary surface complexation, have not been studied thoroughly so far. Moreover, conventionally the
578 adsorption of ions to surfaces of opposite charge is studied. Sorption of anionic actinide complexes to
579 a negatively charged surface, as observed in the present work, is a rarely considered scenario. For
580 example, Yamaguchi et al. (2004) ruled out the sorption of anionic actinide complexes on negatively
581 charged mineral surfaces (pH 11–13.6), but suggested that only neutral actinide species sorbed.

582 A few studies already described the potential of Ca^{2+} to enhance anion retention in general. Allen
583 et al. (2019) and Griffin et al. (2016) described a Ca-bridging between the anionic surfactant bis(2-
584 ethylhexyl) sulfosuccinate and mica surfaces. The bridging effect was only observed in the presence of
585 divalent cations and was absent in monovalent electrolyte solutions. Also Arnarson and Keil (2000)
586 pointed out an increased sorption of natural organic matter to montmorillonite due to Ca-bridging.
587 Furthermore, sorption experiments by Androniuk et al. (2017) revealed a mediating effect of Ca^{2+}
588 between gluconate and C-S-H mineral surfaces, as the retention of the organic molecules strongly
589 depended on the surface charge and Ca^{2+} concentration. For Np(V) and Np(VI), Tits et al. (2014)
590 obtained higher retention on TiO_2 in the presence of Ca^{2+} at pH 13.3. The K_d value of Np(VI)
591 increased by two orders of magnitude upon introduction of 10^{-5} M Ca^{2+} . The authors stated that
592 additional experiments, especially spectroscopy, were necessary to draw conclusions regarding the
593 underlying retention mechanisms.

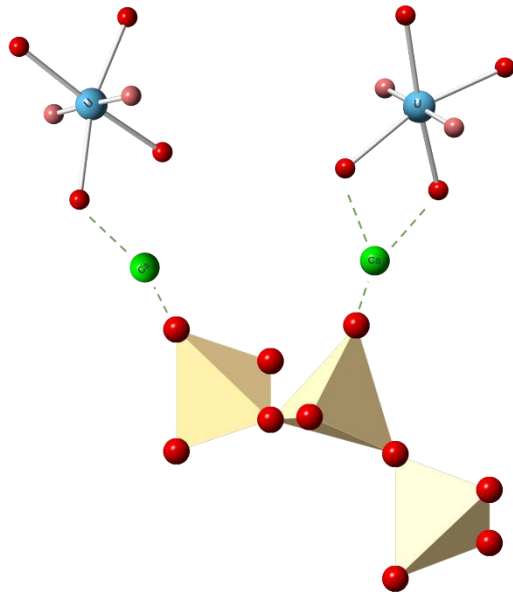
594 The effect of Ca^{2+} on U(VI) adsorption was widely studied in the near-neutral to slightly alkaline
595 pH range: Ca can either sorb to minerals, thus competing with RNs for surface sites, or the presence of
596 Ca^{2+} might affect the aqueous RN speciation by forming stable ternary aqueous complexes (e.g.,
597 $\text{Ca}_2\text{UO}_2(\text{CO}_3)_{3(\text{aq})}$, $\text{CaUO}_2(\text{CO}_3)_3^{2-}$) which show a decreased retention on minerals (Dong et al., 2005;
598 Joseph et al., 2013a; Meleshyn et al., 2009; Philipp et al., 2019; Richter et al., 2016; Stockmann et al.,
599 2022). In contrast, there are only few published and peer reviewed data in the alkaline to hyperalkaline
600 pH range. In the batch sorption data of two Ph.D. theses, a Ca-induced increase in U(VI) sorption at
601 (hyper)alkaline conditions was observed: Schnurr (2015) noticed a difference between U(VI) sorption
602 on Illite du Puy in NaCl and CaCl_2 at pH 10–12. Mayordomo (2017) needed to introduce a Ca-
603 mediated surface complex $\text{S}^{\text{WO}}\text{-Ca-UO}_2(\text{OH})_3$ to be able to model elevated U(VI) sorption on smectite
604 at pH 9.5–10. Only recently, Brix et al. (2021) described an increased U(VI) retention on Ca-bentonite
605 in the presence of Ca^{2+} at pH 12.5 and 13 and proposed a bridging effect of Ca. The results of Philipp
606 et al. (2019) and of the present study also strongly suggest such Ca-mediated surface complexes, even
607 over a wider alkaline pH range.

608 Molecular dynamics (MD) and potential of mean force (PMF) calculations, performed for
609 potential interactions in the system U(VI) – gluconate – C-S-H by Androniuk and Kalinichev (2020),

610 revealed several aspects that are important for the discussion of the proposed complexes in the present
611 paper: (i) the interaction between $\text{UO}_2(\text{OH})_3^-$ and Ca^{2+} ions in solution is strong, showing two main
612 energy minima at interionic distances of $\sim 4.1 \text{ \AA}$ and $\sim 3.6 \text{ \AA}$ that correspond to the formation of one
613 and two OH^- bridges, respectively. The interaction of U(VI) with Ca(OH)^+ and Na^+ is considered
614 weak. (ii) The binding of Ca^{2+} on deprotonated silanol groups of the C-S-H surface is strong, can
615 occur via inner- and outer-sphere coordination, and a relatively high energy is required to replace the
616 bound cation by another ion or molecule. Ca(OH)^+ binding is less favorable. (iii) Compared to Ca^{2+}
617 sorption, the sorption of $\text{CaUO}_2(\text{OH})_3^+$ is weaker. (iv) U(VI) can bind directly to unoccupied
618 deprotonated silanol groups and by the formation of ternary surface complexes between $\text{UO}_2(\text{OH})_3^-$
619 and Ca^{2+} cations sorbed to negatively charged silanol groups on the aqueous C-S-H interface.

620 From these MD simulation results, we derive structures for two ternary surface complexes
621 showing the Ca-bridge between silanol surface sites of the minerals and uranyl hydroxide species
622 ($\text{UO}_2(\text{OH})_3^-$, $\text{UO}_2(\text{OH})_4^{2-}$) that represent our hypothesized retention mechanism (Fig. 9). These
623 structures are further supported by our EXAFS results (Philipp et al., 2019), which demonstrated 4-
624 fold coordination in the equatorial plane of U(VI) for the species. Moreover, the EXAFS results did
625 not allow fitting of the U-Si/Al scattering paths for these species, which is indicative of a larger
626 distance of the U(VI) moiety to the mineral surface. Our current luminescence spectroscopic study
627 provides the so far missing spectroscopic evidence for the existence of such ternary U(VI) surface
628 complexes at hyperalkaline conditions for Ca-bentonite and C-S-H phases, and in the presence of Ca^{2+}
629 also for the clay minerals kaolinite and muscovite (see section 3.3.).

630 In the presence of Sr^{2+} instead of Ca^{2+} , similar surface complexes with Sr-bridges are conceivable
631 since the speciation of Ca^{2+} and Sr^{2+} as a function of pH is very similar, with onset of hydrolysis at
632 about pH 11.5 and dominance of CaOH^+ and SrOH^+ species above pH 13.1 and pH 13.7, respectively.
633 Also for Sr^{2+} , inner-sphere sorption onto illite has been detected above pH 11 (Fuller et al., 2016).



634

635 Figure 9: Proposed structure for ternary surface complexes showing exemplary the Ca-bridge between
 636 silanol surface sites of the minerals and uranyl hydroxide species predominant in the hyperalkaline pH
 637 range (see Fig. S4). Color code: uranium (blue), calcium (green), silicon (yellow), oxygen (red).

638 The second mechanism identified by TRLFS, for how the presence of Ca^{2+} enhances the U(VI)
 639 and Np(VI) immobilization at hyperalkaline conditions, is the formation of Ca-containing secondary
 640 minerals which are able to retain actinides. The contact of clay with hyperalkaline cement pore fluids
 641 results in partial dissolution of clay minerals and subsequent precipitation of secondary minerals such
 642 as calcium (aluminum) silicate hydrates (C-(A-)S-H), whereby also formation of zeolites,
 643 feldspathoids, feldspars and others was shown (Claret et al., 2002; Di Pietro et al., 2020; Fernandez et
 644 al., 2010; Gaucher and Blanc, 2006; Grambow, 2016; Sakamoto et al., 2007; Savage et al., 2007;
 645 Wilson et al., 2021). Enhanced dissolution of quartz, microcline, orthoclase, and albite has been
 646 observed in Ca-containing hyperalkaline solutions (Bagheri et al., 2022). C-(A-)S-H phases have been
 647 shown to form as secondary mineral phases in a so-called pozzolanic reaction in which available free
 648 Ca^{2+} reacts with dissolved mineral components (Bagheri et al., 2022; Cherian et al., 2018). Thus, a
 649 prerequisite for the formation of C-(A-)S-H phases is the partial dissolution of clay and silicate
 650 minerals above pH 10. In leaching tests, we observed significant release of Si and Al from the
 651 muscovite and the synthetic kaolinite at $\text{pH} > 10$. Leaching experiments with Ca-bentonite (Fig. S8)
 652 show a significant release of Si and Al into the solution only above pH 12, suggesting an apparent
 653 stability of the Ca-bentonite between pH 10 and 12. However, given the observed decrease in Ca

654 concentration in solution between pH 10 and 12, Si and Al could already be released from the clay
655 minerals below pH 12, but immediately bound by precipitation of C-(A-)S-H phases. Leached Si and
656 Al then only appear in the supernatant at pH > 12, when the availability of Ca becomes the limiting
657 factor for C-(A-)S-H formation.

658 Due to the often amorphous or semi-crystalline character of C-(A-)S-H phases, their formation is
659 difficult to detect with powder X-ray diffraction, especially when they precipitate as secondary
660 minerals in multi-mineral solids such as bentonite. Weak diffraction signals from evolving C-(A-)S-H
661 phases can easily be superimposed by the diffraction patterns of the primary minerals. Nevertheless, a
662 small but distinct peak ($2\theta = 29.3^\circ$, Cu $K\alpha$) can be observed in the diffractograms of leached Ca-
663 bentonite at pH 12 and 12.5, which is identified as a C-S-H phase by comparison with the
664 diffractogram of the synthetically prepared C-S-H phase with a Ca/Si ratio of 1.2 (Fig. S9).

665 C-(A-)S-H phases show a high sorption capacity for trivalent to hexavalent actinides such as
666 Cm(III), Am(III), Th(IV), Np(IV,V,VI), Pu(IV), and U(VI) (e.g., (Gaona et al., 2011; Häußler et al.,
667 2018; Stumpf et al., 2004; Tits et al., 2014; Tits et al., 2015; Wolter et al., 2019a). C-S-H phase
668 formation in Ca-montmorillonite at pH ≥ 12 with simultaneous incorporation of Cm(III) was
669 previously hypothesized by Rabung et al. (2005). Our current luminescence spectroscopic study
670 provides the spectroscopic evidence for the second retention mechanism in U(VI)-containing clay
671 systems under hyperalkaline conditions, namely U(VI) absorption in the interlayer region of C-(A-)S-
672 H phases, and thus also evidence for the formation of C-(A-)S-H phases in clay mineral systems under
673 hyperalkaline conditions (see section 3.3.).

674 These results are in good agreement with the observed actinide retention on minerals in Ca-
675 containing hyperalkaline solutions.

676 **4. Conclusions**

677 The results show that at (hyper)alkaline conditions, the presence of Ca^{2+} and Sr^{2+} has a major
678 effect on the retention of hexavalent actinides on clay mineral surfaces. Alkaline earth ions can sorb
679 on the mineral, thus, on the one hand, compete with the RNs for binding sites, but, on the other hand,
680 mediate retention of anionic actinide species. While actinide sorption tends to be reduced due to

681 presence of Ca^{2+} in carbonate-containing solutions at neutral or slightly alkaline conditions, the
682 actinide retention is enhanced by Ca at hyperalkaline conditions.

683 Our study verifies the hypothesis that negatively charged species $\text{UO}_2(\text{OH})_3^-$, $\text{UO}_2(\text{OH})_4^{2-}$ and
684 $\text{NpO}_2(\text{OH})_3^-$, $\text{NpO}_2(\text{OH})_4^{2-}$, respectively, bind via Ca^{2+} cations to deprotonated surface groups of the
685 aluminosilicate minerals. Moreover, as a consequence of partial dissolution of the aluminosilicates under
686 hyperalkaline conditions, Ca^{2+} can induce a precipitation of secondary phases such as C-(A)-S-H,
687 which additionally contribute to the retention of anionic actinide species in clayey systems, as
688 demonstrated for the first time for U(VI) by luminescence spectroscopy. A combination of these
689 processes leads to an increased U(VI) and Np(VI) retention at hyperalkaline conditions compared to
690 chemical systems with exclusively monovalent cations in the background electrolytes.

691 In deep geological nuclear waste repositories, Ca^{2+} and other alkaline earth cations are
692 ubiquitously present either in the pore water or as leachable ions in the host rock as well as in cement
693 and bentonite as components of the multi-barrier system and consequently, contribute to the long-term
694 retention of U(VI) and Np(VI) under the geochemical conditions prevailing in the repository. This
695 deeper mechanistic understanding of actinide retention processes at hyperalkaline and high ionic
696 strengths conditions contributes to an improved safety assessment of high-level waste repositories in
697 deep geological formations.

698

699 **CRedit authorship contribution statement**

700 T. Philipp: Investigation, Formal analysis, Validation, Writing – review & editing.

701 N. Huittinen: Investigation, Formal analysis, Methodology, Writing – review & editing.

702 S. Shams Aldin Azzam: Investigation, Formal analysis.

703 R. Stohr: Investigation, Formal analysis.

704 J. Stietz: Investigation, Formal analysis.

705 T. Reich: Funding acquisition, Supervision, Writing – review & editing.

706 K. Schmeide: Conceptualization, Methodology, Funding acquisition, Project administration,

707 Supervision, Writing – review & editing.

708

709 **Declaration of competing interest**

710 The authors declare that they have no known competing financial interests or personal relationships
711 that could have appeared to influence the work reported in this paper.

712

713 **Acknowledgements**

714 The authors thank Samer Amayri (JGU Mainz) and Sabrina Beutner (HZDR) for ICP-MS analyses.

715

716 **Funding**

717 This work was supported by the German Federal Ministry for Economic Affairs and Energy (BMWi)
718 within the projects GRaZ (no. 02E11415A, 02E11415B) and GRaZ II (no. 02E11860B).

719

720 **Appendix A. Supplementary data**

721 Supplementary data to this article can be found online at

722

723 **References**

724 Allen, F.J., Truscott, C.L., Gutfreund, P., Welbourn, R.J.L. and Clarke, S.M. (2019) Potassium, calcium, and
725 magnesium bridging of AOT to mica at constant ionic strength. *Langmuir* 35, 5753-5761.

726 Amayri, S., Jermolajev, A. and Reich, T. (2011) Neptunium(V) sorption on kaolinite. *Radiochim. Acta* 99, 349-
727 357.

728 Androniuk, I. and Kalinichev, A.G. (2020) Molecular dynamics simulation of the interaction of uranium(VI) with
729 the C-S-H phase of cement in the presence of gluconate. *Appl. Geochem.* 113, 104496.

730 Androniuk, I., Landesman, C., Henocq, P. and Kalinichev, A.G. (2017) Adsorption of gluconate and uranyl on C-S-
731 H phases: Combination of wet chemistry experiments and molecular dynamics simulations for the binary
732 systems. *Phys. Chem. Earth* 99, 194-203.

733 Arnarson, T.S. and Keil, R.G. (2000) Mechanisms of pore water organic matter adsorption to montmorillonite.
734 *Marine Chem.* 71, 309-320.

735 Atesok, G., Somasundaran, P. and Morgan, L.J. (1988) Adsorption properties of Ca²⁺ on Na-kaolinite and its
736 effect on flocculation using polyacrylamides. *Colloid Surface* 32, 127-138.

737 Bagheri, M., Lothenbach, B., Shakoorioskooie, M. and Scrivener, K. (2022) Effect of different ions on dissolution
738 rates of silica and feldspars at high pH. *Cement Concrete Res.* 152, 106644.

739 Berner, U.R. (1992) Evolution of pore water chemistry during degradation of cement in a radioactive waste
740 repository environment. *Waste Manage.* 12, 201-219.

- 741 Bradl, H. (2005) *Heavy Metals in the Environment: Origin, Interaction and Remediation*, 1st Edition ed. Elsevier
742 Academic Press, London, UK.
- 743 Brix, K., Baur, S., Haben, A. and Kautenburger, R. (2021) Building the bridge between U(VI) and Ca-bentonite –
744 Influence of concentration, ionic strength, pH, clay composition and competing ions. *Chemosphere* 285,
745 131445.
- 746 Chen, X., Peng, S. and Wang, J. (2014) Retention profile and kinetics characteristics of the radionuclide 90-Sr(II)
747 onto kaolinite. *J. Radioanal. Nucl. Chem.* 303, 509-519.
- 748 Cherian, C., Kollannur, N.J., Bandipally, S. and Arnepalli, D.N. (2018) Calcium adsorption on clays: Effects of
749 mineralogy, pore fluid chemistry and temperature. *Appl. Clay Sci.* 160, 282-289.
- 750 Claret, F., Bauer, A., Schäfer, T., Griffault, L. and Lanson, B. (2002) Experimental investigation of the interaction
751 of clays with high-pH solutions: A case study from the Callovo-Oxfordian formation, Meuse-Haute Marne
752 underground laboratory (France). *Clay Clay Miner.* 50, 633-646.
- 753 Di Pietro, S., Emerson, H.P., Katsenovich, Y., Qafoku, N.P. and Szecsod, J. (2020) Phyllosilicate mineral
754 dissolution upon alkaline treatment under aerobic and anaerobic conditions. *Appl. Clay Sci.* 189, 105520.
- 755 Dong, W.M., Ball, W.P., Liu, C.X., Wang, Z.M., Stone, A.T., Bai, J. and Zachara, J.M. (2005) Influence of calcite
756 and dissolved calcium on uranium(VI) sorption to a Hanford subsurface sediment. *Environ. Sci. Technol.* 39,
757 7949-7955.
- 758 Farooq, U., Tweheyo, M.T., Sjöblom, J. and Øye, G. (2011) Surface characterization of model, outcrop, and
759 reservoir samples in low salinity aqueous solutions. *J. Disper. Sci. Technol.* 32, 519-531.
- 760 Fellhauer, D., Gaona, X., Rothe, J., Altmaier, M. and Fanghänel, T. (2018) Neptunium(VI) solubility in alkaline
761 CaCl₂ solutions: evidence for the formation of calcium neptunates Ca_xNpO_{3+x}(s,hyd). *Monatsh. Chem.* 149, 237-
762 252.
- 763 Fenter, P., Park, C., Nagy, K.L. and Sturchio, N.C. (2007) Resonant anomalous X-ray reflectivity as a probe of ion
764 adsorption at solid–liquid interfaces. *Thin Solid Films* 515, 5654-5659.
- 765 Fernandez, R., Rodriguez, M., de la Villa, R.V. and Cuevas, J. (2010) Geochemical constraints on the stability of
766 zeolites and C-S-H in the high pH reaction of bentonite. *Geochim. Cosmochim. Acta* 74, 890-906.
- 767 Fialips, C.-I., Petit, S., Decarreau, A. and Beaufort, D. (2000) Influence of synthesis pH on kaolinite "crystallinity"
768 and surface properties. *Clay Clay Miner.* 48, 173-184.
- 769 Fuller, A.J., Shaw, S., Peacock, C.L., Trivedi, D. and Burke, I.T. (2016) EXAFS study of Sr sorption to illite,
770 goethite, chlorite, and mixed sediment under hyperalkaline conditions. *Langmuir* 32, 2937-2946.
- 771 Gaona, X., Dähn, R., Tits, J., Scheinost, A.C. and Wieland, E. (2011) Uptake of Np(IV) by C-S-H phases and
772 cement paste: An EXAFS study. *Environ. Sci. Technol.* 45, 8765-8771.
- 773 Gaucher, E.C. and Blanc, P. (2006) Cement/clay interactions - A review: Experiments, natural analogues, and
774 modeling. *Waste Manage.* 26, 776-788.
- 775 Gaucher, E.C., Blanc, P., Bardot, F., Braibant, G., Buschaert, S., Crouzet, C., Gautier, A., Girard, J.P., Jacquot, E.,
776 Lassin, A., Negrel, G., Tournassat, C., Vinsot, A. and Altmann, S. (2006) Modelling the porewater chemistry of
777 the Callovian-Oxfordian formation at a regional scale. *C. R. Geosci.* 338, 917-930.
- 778 Grambow, B. (2016) Geological disposal of radioactive waste in clay. *Elements* 12, 239-245.
- 779 Griffin, L.R., Browning, K.L., Lee, S.Y., Skoda, M.W., Rogers, S. and Clarke, S.M. (2016) Multilayering of calcium
780 aerosol-OT at the mica/water interface studied with neutron reflection: Formation of a condensed lamellar
781 phase at the CMC. *Langmuir* 32, 13054-13064.

- 782 Häußler, V., Amayri, S., Beck, A., Platte, T., Stern, T.A., Vitova, T. and Reich, T. (2018) Uptake of actinides by
783 calcium silicate hydrate (C-S-H) phases. *Appl. Geochem.* 98, 426-434.
- 784 He, Y., Chen, Y.-G. and Ye, W.-M. (2016) Equilibrium, kinetic, and thermodynamic studies of adsorption of Sr(II)
785 from aqueous solution onto GMZ bentonite. *Environ. Earth Sci.* 75, 807.
- 786 Hellebrandt, S. (2017) Grenzflächenreaktionen von Actiniden an Muskovit. Ph.D. thesis, Technische Universität
787 Dresden, Dresden, Germany.
- 788 Hennig, T., Stockmann, M. and Kühn, M. (2020) Simulation of diffusive uranium transport and sorption
789 processes in the Opalinus Clay. *Appl. Geochem.* 123, 104777.
- 790 Hink, M.A., Visser, N.V., Borst, J.W., van Hoek, A. and Visser, A.J.W.G. (2003) Practical use of corrected
791 fluorescence excitation and emission spectra of fluorescent proteins in Förster Resonance Energy Transfer
792 (FRET) studies. *J. Fluoresc.* 13, 185-188.
- 793 Ho, C. and Handy, R.L. (1963) Electrokinetic properties of lime-treated bentonites. *Clay Clay Miner.* 12, 267-280.
- 794 Hubbard, A.T. (2002) *Encyclopedia of Surface and Colloid Science*. Dekker, New York (USA); Basel (Switzerland).
- 795 Huittinen, N., Rabung, T., Andrieux, P., Lehto, J. and Geckeis, H. (2010) A comparative batch sorption and time-
796 resolved laser fluorescence spectroscopy study on the sorption of Eu(III) and Cm(III) on synthetic and natural
797 kaolinite. *Radiochim. Acta* 98, 613-620.
- 798 Jenni, A., Wersin, P., Thoenen, T., Baeyens, B., Ferrari, A., Gimmi, T., Mäder, U., Marschall, P., Hummel, W. and
799 Leupin, O. (2019) Bentonite backfill performance in a high-level waste repository: a geochemical perspective.
800 Nagra Technical Report 19-03, Nagra, Wettingen, Switzerland.
- 801 Joseph, C., Mibus, J., Trepte, P., Müller, C., Brendler, V., Park, D.M., Jiao, Y., Kersting, A.B. and Zavarin, M.
802 (2017) Long-term diffusion of U(VI) in bentonite: Dependence on density. *Sci. Total Environ.* 575, 207-218.
- 803 Joseph, C., Stockmann, M., Schmeide, K., Sachs, S., Brendler, V. and Bernhard, G. (2013a) Sorption of U(VI) onto
804 Opalinus Clay: Effects of pH and humic acid. *Appl. Geochem.* 36, 104-117.
- 805 Joseph, C., Van Loon, L.R., Jakob, A., Steudtner, R., Schmeide, K., Sachs, S. and Bernhard, G. (2013b) Diffusion of
806 U(VI) in Opalinus Clay: Influence of temperature and humic acid. *Geochim. Cosmochim. Acta* 109, 74-89.
- 807 Kaufhold, S. and Dohrmann, R. (2016) Distinguishing between more and less suitable bentonites for storage of
808 high-level radioactive waste. *Clay Min.* 51, 289-302.
- 809 Kowal-Fouchard, A., Drot, R., Simoni, E. and Ehrhardt, J. (2004) Use of spectroscopic techniques for
810 uranium(VI)/montmorillonite interaction modeling. *Environ. Sci. Technol.* 38, 1399-1407.
- 811 Kremleva, A., Krüger, S. and Rösch, N. (2020) Uranyl(VI) sorption in calcium silicate hydrate phases. A quantum
812 chemical study of tobermorite models. *Appl. Geochem.* 113, 104463.
- 813 Lommerzheim, M. and Jobmann, A. (2014) Endlagerkonzept sowie Verfüll- und Verschlusskonzept für das
814 Standortmodell NORD, TEC-08-2014-Z. DBE Technology, Peine, Germany.
- 815 Marques Fernandes, M., Baeyens, B., Dähn, R., Scheinost, A.C. and Bradbury, M.H. (2012) U(VI) sorption on
816 montmorillonite in the absence and presence of carbonate: A macroscopic and microscopic study. *Geochim.
817 Cosmochim. Acta* 93, 262-277.
- 818 Marsac, R., Banik, N.L., Lützenkirchen, J., Diascorn, A., Bender, K., Marquardt, C.M. and Geckeis, H. (2017)
819 Sorption and redox speciation of plutonium at the illite surface under highly saline conditions. *J. Colloid
820 Interface Sci.* 485, 59-64.

- 821 Mayordomo, N. (2017) Experimental and theoretical studies of mixed smectite and Al₂O₃ nanoparticles to
 822 improve pollutant retention in geochemical barriers. Ph.D. thesis, Departamento de Química Analítica, Química
 823 Física e Ingeniería Química. Universidad de Alcalá, Madrid, Spain.
- 824 Meleshyn, A., Azeroual, M., Reeck, T., Houben, G., Riebe, B. and Bunnenberg, C. (2009) Influence of (calcium-
 825)uranyl-carbonate complexation on U(VI) sorption on Ca- and Na-bentonites. *Environ. Sci. Technol.* 43, 4896–
 826 4901.
- 827 Missana, T. and García-Gutiérrez, M. (2007) Adsorption of bivalent ions (Ca(II), Sr(II) and Co(II)) onto FEBEX
 828 bentonite. *Phys. Chem. Earth, Parts A/B/C* 32, 559-567.
- 829 Missana, T., Garcia-Gutierrez, M. and Alonso, U. (2008) Sorption of strontium onto illite/smectite mixed clays.
 830 *Phys. Chem. Earth, Parts A/B/C* 33, S156-S162.
- 831 Nagasaki, S., Saito, T. and Yang, T.T. (2016) Sorption behavior of Np(V) on illite, shale and MX-80 in high ionic
 832 strength solutions. *J. Radioanal. Nucl. Chem.* 308, 143-153.
- 833 Nowak, T. and Maßmann, J. (2013) Endlagerstandortmodell Nord (AnSichT) - Teil III: Auswahl von Gesteins- und
 834 Fluideigenschaften für numerische Modellberechnungen im Rahmen des Langzeitsicherheitsnachweises.
 835 Bundesanstalt für Geowissenschaften und Rohstoffe (BGR), Hannover, Germany.
- 836 OECD/NEA (2020) Management and Disposal of High-Level Radioactive Waste: Global Progress and Solutions,
 837 Radioactive Waste Management, OECD Publishing, Paris, <https://doi.org/10.1787/33f65af2-en>.
- 838 Olivelli, M.S., Curutchet, G.A. and Sanchez, R.M.T. (2013) Uranium uptake by montmorillonite-biomass
 839 complexes. *Ind. Eng. Chem. Res.* 52, 2273-2279.
- 840 Philipp, T., Shams Aldin Azzam, S., Rossberg, A., Huittinen, N., Schmeide, K. and Stumpf, T. (2019) U(VI) sorption
 841 on Ca-bentonite at (hyper)alkaline conditions - Spectroscopic investigations of retention mechanisms. *Sci. Total*
 842 *Environ.* 676, 469-481.
- 843 Pointeau, I., Reiller, P., Mace, N., Landesman, C. and Coreau, N. (2006) Measurement and modeling of the
 844 surface potential evolution of hydrated cement pastes as a function of degradation. *J. Colloid Interface Sci.* 300,
 845 33-44.
- 846 Pruet, R.J. and Webb, H.L. (1993) Sampling and analysis of KGa-1b well-crystallized kaolin source clay. *Clay Clay*
 847 *Miner.* 41, 514-519.
- 848 Rabung, T., Pierret, M.C., Bauer, A., Geckeis, H., Bradbury, M.H. and Baeyens, B. (2005) Sorption of
 849 Eu(III)/Cm(III) on Ca-montmorillonite and Na-illite. Part 1: Batch sorption and time-resolved laser fluorescence
 850 spectroscopy experiments. *Geochim. Cosmochim. Acta* 69, 5393-5402.
- 851 Richter, C., Müller, K., Drobot, B., Steudtner, R., Großmann, K., Stockmann, M. and Brendler, V. (2016)
 852 Macroscopic and spectroscopic characterization of uranium(VI) sorption onto orthoclase and muscovite and
 853 the influence of competing Ca²⁺. *Geochim. Cosmochim. Acta* 189, 143-157.
- 854 Sakamoto, H., Shibata, M., Owada, H., Kaneko, M., Kuno, Y. and Asano, H. (2007) Development of an analytical
 855 technique for the detection of alteration minerals formed in bentonite by reaction with alkaline solutions. *Phys.*
 856 *Chem. Earth* 32, 311-319.
- 857 Savage, D., Walker, C., Arthur, R., Rochelle, C., Oda, C. and Takase, H. (2007) Alteration of bentonite by
 858 hyperalkaline fluids: A review of the role of secondary minerals. *Phys. Chem. Earth* 32, 287-297.
- 859 Schlegel, M.L., Nagy, K.L., Fenter, P., Cheng, L., Sturchio, N.C. and Jacobsen, S.D. (2006) Cation sorption on the
 860 muscovite (001) surface in chloride solutions using high-resolution X-ray reflectivity. *Geochim. Cosmochim.*
 861 *Acta* 70, 3549-3565.

- 862 Schmeide, K. and Bernhard, G. (2010) Sorption of Np(V) and Np(IV) onto kaolinite: Effects of pH, ionic strength,
863 carbonate and humic acid. *Appl. Geochem.* 25, 1238-1247.
- 864 Schnurr, A. (2015) Untersuchungen zur RadionuklidSORPTION an Tonmineraloberflächen bei hohen
865 Ionenstärken. Ph.D. thesis, Karlsruher Institut für Technologie (KIT), Karlsruhe, Germany.
- 866 Schnurr, A., Marsac, R., Rabung, T., Lützenkirchen, J. and Geckeis, H. (2015) Sorption of Cm(III) and Eu(III) onto
867 clay minerals under saline conditions: Batch adsorption, laser-fluorescence spectroscopy and modeling.
868 *Geochim. Cosmochim. Acta* 151, 192-202.
- 869 Scholze, R., Amayri, S. and Reich, T. (2019) Modeling the sorption of Np(V) on Na-montmorillonite - effects of
870 pH ionic strength and CO₂. *Radiochim. Acta* 107, 615-622.
- 871 Stockmann, M., Fritsch, K., Bok, F., Marques Fernandes, M., Baeyens, B., Steudtner, R., Müller, K., Nebelung, C.,
872 Brendler, V., Stumpf, T. and Schmeide, K. (2022) New insights into U(VI) sorption onto montmorillonite from
873 batch sorption and spectroscopic studies at increased ionic strength. *Sci. Total Environ.* 806, 150653.
- 874 Stumpf, T., Tits, J., Walther, C., Wieland, E. and Fanghänel, T. (2004) Uptake of trivalent actinides (curium(III))
875 by hardened cement paste: a time-resolved laser fluorescence spectroscopy study. *J. Colloid Interf. Sci.* 276,
876 118-124.
- 877 Sugiura, Y., Ishidera, T. and Tachi, Y. (2021) Surface complexation of Ca and competitive sorption of divalent
878 cations on montmorillonite under alkaline conditions. *Appl. Clay Sci.* 200, 105910.
- 879 Szymanek, K., Charnas, R. and Piasecki, W. (2021) Investigations of mechanism of Ca²⁺ adsorption on silica and
880 alumina based on Ca-ISE monitoring, potentiometric titration, electrokinetic measurements and surface
881 complexation modeling. *Adsorption* 27, 105-115.
- 882 Tits, J., Gaona, X., Laube, A. and Wieland, E. (2014) Influence of the redox state on the neptunium sorption
883 under alkaline conditions: Batch sorption studies on titanium dioxide and calcium silicate hydrates. *Radiochim.*
884 *Acta* 102, 385-400.
- 885 Tits, J., Geipel, G., Macé, N., Eilzer, M. and Wieland, E. (2011) Determination of uranium(VI) sorbed species in
886 calcium silicate hydrate phases: A laser-induced luminescence spectroscopy and batch sorption study. *J. Colloid*
887 *Interface Sci.* 359, 248-256.
- 888 Tits, J., Walther, C., Stumpf, T., Mace, N. and Wieland, E. (2015) A luminescence line-narrowing spectroscopic
889 study of the uranium(VI) interaction with cementitious materials and titanium dioxide. *Dalton Trans.* 44, 966-
890 976.
- 891 Tran, E.L., Teutsch, N., Klein-BenDavid, O. and Weisbrod, N. (2018) Uranium and cesium sorption to bentonite
892 colloids under carbonate-rich environments: Implications for radionuclide transport. *Sci. Total Environ.* 643,
893 260-269.
- 894 Viallis-Terrisse, H., Nonat, A. and Petit, J.-C. (2001) Zeta-potential study of calcium silicate hydrates interacting
895 with alkaline cations. *J. Colloid Interface Sci.* 244, 58-65.
- 896 Wieland, E., Wanner, H., Albinsson, Y., Wersin, P. and Karnland, O. (1994) A surface chemical model of the
897 bentonite-water interface and its implications for modelling the near field chemistry in a repository for spent
898 fuel. Swedish Nuclear Fuel and Waste Management Company (SKB), Stockholm, Sweden.
- 899 Wilson, J., Bateman, K. and Tachi, Y. (2021) The impact of cement on argillaceous rocks in radioactive waste
900 disposal systems: A review focusing on key processes and remaining issues. *Appl. Geochem.* 130, 104979.
- 901 Wolfgramm, M., Thorwart, K., Rauppach, K. and Brandes, J. (2011) Zusammensetzung, Herkunft und Genese
902 geothermaler Tiefengrundwässer im Norddeutschen Becken (NDB) und deren Relevanz für die geothermische
903 Nutzung. *Z. Geol. Wissenschaft* 339, 173-193.

- 904 Wolter, J.-M., Schmeide, K., Huittinen, N. and Stumpf, T. (2019a) Cm(III) retention by calcium silicate hydrate
905 (C-S-H) gel and secondary alteration phases in carbonate solutions with high ionic strength: A site-selective
906 TRLFS study. *Sci. Rep.* 9, 14255.
- 907 Wolter, J.-M., Schmeide, K., Weiss, S., Bok, F., Brendler, V. and Stumpf, T. (2019b) Stability of U(VI) doped
908 calcium silicate hydrate gel in repository-relevant brines studied by leaching experiments and spectroscopy.
909 *Chemosphere* 218, 241-251.
- 910 Wu, T., Amayri, S., Drebert, J., Van Loon, L.R. and Reich, T. (2009) Neptunium(V) sorption and diffusion in
911 Opalinus Clay. *Environ. Sci. Technol.* 43, 6567-6571.
- 912 Yamaguchi, T., Nakayama, S. and Yoshida, T. (2004) Interactions between anionic complex species of actinides
913 and negatively charged mineral surfaces. *Radiochim. Acta* 92, 677-682.
- 914