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1 **Neptunium(V) transport in granitic rock: A laboratory scale study on the influence of**
2 **bentonite colloids**

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4 O. Elo^{1*}, P. Hölttä¹, P. Kekäläinen¹, M. Voutilainen¹, N. Huittinen²

5 ¹ Department of Chemistry, Radiochemistry, University of Helsinki, P.O. Box 55, FIN-00014

6 University of Helsinki, Finland

7 ²Helmholz-Zentrum Dresden-Rossendorf, Institute of Resource Ecology, Bautzner Landstr.

8 400, 01328, Dresden, Germany

9

10 *corresponding author

11 e-mail: outi.elo@helsinki.fi

12 **Abstract**

13 In the present study neptunium(V) uptake by crystalline granitic rock (Kuru Grey granite) and the
14 role of stable and mobile bentonite colloids (MX-80) on the migration of neptunium(V) was
15 investigated. Two different experimental setups were utilized, batch-type experiments under
16 stagnant conditions and column experiments under flowing water conditions. The uptake of 10^{-6} M
17 neptunium(V) by 40 g/L crushed granite in 10 mM NaClO₄ was found to be pH-dependent, whereas
18 neptunium(V) uptake by MX-80 bentonite colloids (0.08-0.8 g/L) was pH-independent up to a pH-
19 value of approximately 11. Column experiments were conducted in the presence and absence of
20 colloids at two pH values (pH = 8 and 10) and two flow rates (0.3 and 0.8 mL/h) in 10 mM NaClO₄.
21 The injected neptunium(V) concentration was 2×10^{-4} M and the colloid concentration ranged from
22 0.08 – 0.32 g/L. The properties of the flow field in the columns were investigated with a
23 conservative chloride tracer, at the same two flow rates of 0.8 and 0.3 mL/h. The resulting
24 breakthrough curves were modeled using the analytical solution of advection–matrix diffusion
25 equation. A tailing of neptunium(V) breakthrough curves in comparison to the conservative tracer
26 was observed, which could be explained by a slightly higher retardation of neptunium(V) in the
27 column caused by sorption on the granite. The sorption was in general lower at pH 8 than at pH 10.
28 In addition, the tailing was almost identical in the absence and presence of MX-80 bentonite
29 colloids, implying that the influence of colloids on the neptunium(V) mobility is almost negligible.

30

31 **Keywords:** *Neptunium(V); Bentonite colloids, Granitic rock, Sorption; Column experiments*

32

33 **Highlights**

- 34 ■ The influence of MX-80 bentonite colloids on neptunium(V) migration in granitic media
35 was investigated.
- 36 ■ Sorption of neptunium(V) on granite was found to be pH-dependent, while MX-80 colloids
37 showed a pH-independent uptake of neptunium(V).
- 38 ■ Neptunium(V) migration in the absence and presence of MX-80 bentonite colloids was
39 investigated in solid granite drill core columns.
- 40 ■ Drill core column experiments were modeled using the analytical solution of advection–
41 matrix diffusion equation in cylindrical coordinates.
- 42 ■ A clear influence of bentonite colloids on neptunium(V) breakthrough was not observed.
43

44 1 INTRODUCTION

45 Several studies have shown that colloid-facilitated transport of radionuclides could have a
46 significant impact on radionuclide migration from hazardous waste sites (Buddemeier and Hunt,
47 1988; Hursthouse et al., 1991; Kersting et al., 1999; Novikov et al., 2006) and from natural uranium
48 deposits (Short et al., 1988; Vilks et al., 1993). The influence of smectite colloids on the migration
49 of radionuclides in a granitic fracture zone in has been investigated within the Colloid and
50 Radionuclide Retardation experiment (CRR) and the Colloid Formation and Migration (CFM)
51 project (Geckeis et al., 2004; Schäfer et al, 2012; Huber et al., 2011). Laboratory-scale experiments
52 have further shown that the transport of various cationic and anionic metals in porous and fractured
53 media are influenced by the presence of colloids (Ryan and Elimelech, 1996; Artinger et al., 1998;
54 Puls and Powell 1992; Torok et al., 1990; Buckau et al., 2000; Vilks and Baik, 2001; Alonso et al.,
55 2006) depending on the colloid particle size, ground water composition, flow rate, ionic strength,
56 and quantity.

57 Colloids in natural waters are generated by erosion, geochemical alteration of minerals and through
58 precipitation (Degueldre, 1996). In addition, colloids could form from various natural and
59 engineered barriers in future nuclear waste repositories through erosion of the bentonite clay buffer,
60 copper or steel containers, grouting materials, and the uranium fuel itself (Laaksoharju and Wold,
61 2005; Finn et al., 1994; Missana et al., 2003; Baik et al., 2007). In this context, several studies have
62 been conducted, both in the absence and presence of colloids, to understand the migration of
63 various radioactive contaminants under future repository conditions and to gain an insight into the
64 potential role of colloids as mobile solid phases for enhanced radionuclide transport in the
65 geosphere.

66 In the following discussion we will focus on the role of bentonite colloids on radionuclide
67 migration. Bentonite is an important part of engineered barrier systems (EBS) and will be used
68 either as single phase or mixed phase (typically mixed with rock or sand) buffer and backfill

69 material in different repository concepts for spent nuclear fuel (SNF) (Hummel, 2008). Bentonite
70 has been chosen as an EBS component due to favorable properties such as a low hydraulic
71 conductivity, its swelling ability, and high specific surface area allowing for efficient uptake of
72 potential released radionuclides from the SNF (Missana et al., 2003; 2011). Drawbacks of the buffer
73 material are related to its sensitivity towards the overall salt content of the ground water, where
74 colloid generation has been shown to occur for ionic strengths below the critical coagulation
75 concentration (CCC) (García-García et al., 2007; Tombácz and Szekeres, 2004; Lagaly and
76 Ziesmer, 2003). Such ionic strengths and the subsequent formation of stable and mobile bentonite
77 colloids from the EBS could be reached when the meltwater dilutes the ground water after a
78 possible glacial period. A combination of mobile bentonite colloids and their strong sorption
79 capacity may lead to an unwanted, enhanced mobility of released radionuclides in the geosphere. In
80 general, strong retention on the clay material has been demonstrated for radionuclides in the tri- and
81 tetravalent oxidation states (Zhao et al. (2008), Huber et al. (2011), Verma et al. (2014), Begg et al.
82 (2015)), while sorption of hexavalent radionuclides, such as uranium(VI), occurs readily but seems
83 to depend on both the bentonite material as well as the solution conditions (Missana et al. (2004),
84 Bachmaf et al. (2008), Ren et al. (2010), Huber et al. (2011), Zong et al. (2015)). Uptake studies
85 conducted with pentavalent actinides such as neptunium(V) or plutonium(V) are rather scarce,
86 however, sorption isotherm data show that moderate uptake of neptunium(V)/plutonium(V) occurs
87 in the alkaline pH range (Sabodina et al. (2006), Begg et al. (2015), Li et al. (2015)) and that
88 sorption can be enhanced in the presence of Fe-impurities in the bentonite solid (Verma et al.
89 (2017)). In addition to the batch-type experiments, an enhanced radionuclide mobility due to the
90 presence of bentonite colloids under flowing ground water conditions has been observed to take
91 place for tri- and tetravalent radionuclides and their inactive analogues (Möri et al. (2003), Schäfer
92 et al. (2004), Geckeis et al. (2004), Missana et al. (2008), Dittrich et al. (2015)). The situation is
93 very different for both neptunium(V) and uranium(VI), where close to no impact of bentonite

94 colloids on the breakthrough properties of these radioelements has been found (Möri et al. (2003),
95 Schäfer et al. (2004), Geckeis et al. (2004)). For both radionuclides an inconclusive breakthrough
96 behavior, requiring more interpretation, was found in Möri et al. (2003), while the breakthrough of
97 both elements investigated in Geckeis et al. (2004) was faster than observed for the conservative
98 tracer (I). It was assumed that the rapid flow through open channels did not allow for sufficient
99 interaction between the tracers and rock surface. Further attempts to explain neptunium(V)
100 migration through fractured rock in the presence of colloids have, to our knowledge, not been made,
101 implying that definite conclusions about the fate of neptunium in the presence of colloids cannot be
102 drawn. As Np-237, due to its long half-life (2.144×10^6 a), is considered as a significant dose
103 contributor in the SNF repository after 100 000 years (Hursthouse et al., 1991; Kaszuba and Runde,
104 1999; Zhao et al., 2014), understanding the migration behavior of neptunium(V) and the potential
105 influence of colloid transport in the geosphere is mandatory.

106 Thus, the present study aims at describing neptunium(V) uptake by crystalline granitic rock and
107 bentonite colloids under stagnant conditions in batch-type experiments and the role of stable and
108 mobile bentonite colloids on the migration of neptunium(V) through intact granite rock columns
109 under flowing water conditions. The materials used in this study are bentonite colloids prepared
110 from MX-80 bentonite and Kuru Grey granitic rock. Neptunium(V) sorption on these solid phases
111 under stagnant conditions was studied as a function of pH, solid concentration, and neptunium(V)
112 concentration. The column experiments were conducted under ambient air both in the absence and
113 presence of bentonite colloids. The drill core column experiments were modeled using an analytical
114 solution of advection–matrix diffusion equation. The modeling aims at describing the flow field in
115 the experiments in order to better understand the behavior and interaction of neptunium(V) with the
116 rock matrix and the bentonite colloids.

117 2 MATERIALS AND METHODS

118 2.1 MX-80 colloids

119 The MX-80 bentonite used in this study is sodium-rich Wyoming Volclay-type bentonite provided
120 by B⁺Tech. The bentonite has been thoroughly characterized by Kumpulainen and Kiviranta (2010)
121 and it was used as a source of bentonite colloids in the present study. The clay consists of 79.1 %
122 smectite, 7.5 % muscovite, 4.4 % quartz, 3.1 % calcite, 1.7 % plagioclase and minor amounts of
123 other accessory minerals (Kumpulainen and Kiviranta, 2010). The cation exchange capacity (CEC)
124 is 0.89 eq/kg (Kumpulainen and Kiviranta, 2010) and the BET surface area was measured to be
125 28.9 m²/g (this study). The chemical composition and CEC were analyzed from the solid Volclay
126 bentonite powder, hence, slight differences in both the chemical composition and the CEC of the
127 colloid suspension used in this study may exist. The elemental composition of the MX-80 bentonite
128 colloidal fraction (25-450 nm) has been analyzed earlier by Lahtinen et al. (2010) using ICP-MS.
129 The calcium concentration was below limit of quantitation suggesting a homoionic form (Na⁺) of
130 the colloid suspension.

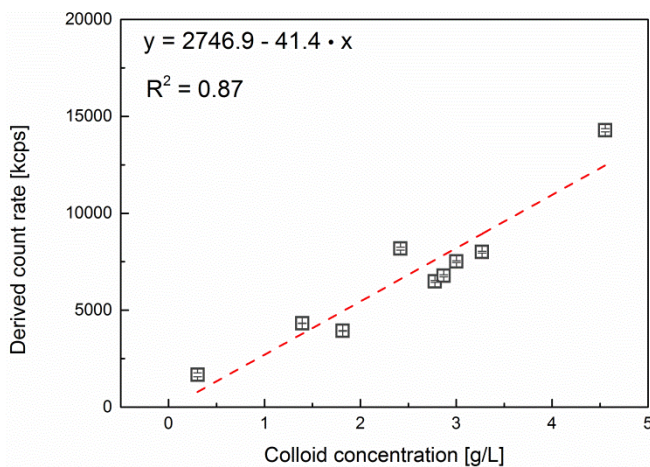
131 The MX-80 colloid solutions were prepared by mixing 5 g of solid MX-80 bentonite powder and
132 500 mL of 10 mM NaClO₄. In batch sorption experiments where a constant pH was required, the 10
133 mM NaClO₄ background electrolyte was buffered either to pH 8 with 10 mM TRIS (tris-
134 hydroxymethyl-aminomethane), or to pH 9 or 10 with 10 mM CHES
135 ((cyclohexylamino)ethanesulfonic acid). Buffered solutions were prepared before addition of MX-
136 80 bentonite to avoid changes in colloid stability caused by changes in ionic strength and pH.
137 Therefore, each colloid suspension was prepared individually leading to dissimilar colloid
138 concentrations in the different batch sorption experiments. In the column experiments, a buffer was
139 not used. The electrolyte solution was in a sealed flask and the pH was checked daily (except during
140 the weekend) and re-adjusted if necessary. The outflow solution in the fraction collector was in

141 contact with ambient air. The pH of the outflow solution was measured before the experiments from
142 the solution collected in a sealed bottle.

143 All bentonite suspensions were allowed to equilibrate under constant shaking for 7 days prior to
144 extraction of the colloidal material. After the equilibration time, the colloidal material was separated
145 by centrifuging the MX-80 solutions for 20 minutes at 12000 x g (12000 rpm). The centrifugation
146 procedure removed particles with a diameter greater than 500 nm, resulting in a mean colloid
147 particle diameter of approximately 200-300 nm, as confirmed by Photon Correlation Spectroscopy
148 (PCS). Both the colloid particle size and the colloid concentration were determined from the
149 centrifuged supernatants. The determination of the colloid concentration is described in the
150 following paragraph.

151 To ensure that the colloids remain stable under the chosen experimental conditions, their stability in
152 10 mM NaClO₄ at around pH 8 without a buffer was followed during 53 days. Five parallel samples
153 were sealed in cuvettes for size or Zeta-potential measurements to avoid the effect of CO₂. The
154 colloid particle size distribution and zeta potential were analyzed applying PCS and
155 microelectrophoresis, respectively (Malvern Zetasizer Nano ZS). During the first 30 days, the mean
156 particle diameter was 215 ± 54 nm. Considering the whole follow-up time, the mean particle
157 diameter was 384 ± 87 nm, the mean colloid concentration was 0.13 ± 0.04 g/L and the mean zeta
158 potential value -54.9 ± -6.6 mV, indicating the existence of a stable bentonite colloid dispersion.
159 The colloid concentration, fed through the column and the eluted amount of colloids in the colloid
160 breakthrough fractions was estimated from the PCS measurement parameter “derived count rate”
161 based on the equation given in Fig. 1 (Niemiaho, 2013). In the calibration curve, the colloid
162 concentration was back-calculated from the structural formula of MX-80 based on the aluminum
163 concentration in bentonite colloid dispersions determined with ICP-MS (Agilent 7500ce). The
164 derived count rate is roughly proportional to the concentration of particles and can be used to
165 estimate the relative concentration of colloids even though the correlation between the ICP-MS and

166 PCS measurements in range < 1g/L is rather uncertain. PCS was also used to follow the overall
167 colloid particle size eluted from the columns.



168

169 Fig. 1. The correlation between the PCS count rate and the colloid concentration calculated from the
170 aluminum content in bentonite analyzed using ICP-MS (Niemiaho, 2013).

171 2.2 Kuru Grey granite

172 Kuru Grey granite was obtained from Kuru Quarry, Tampereen kovakivi Oy, Finland and it has
173 previously been characterized by Hölttä et al. (2004, 2008). The rock matrix of Kuru Grey granite is
174 intact, fine-grained, non-foliated, and equigranular with a density of 2660 kg/m³. It is composed of
175 36% potassium feldspar, 35% quartz, 21% plagioclase, and 8% amphibole and micas. The total
176 porosity of the granite is 0.47 % as determined by Jokelainen et al. 2009. For the neptunium(V)
177 batch sorption studies the Kuru Grey granite was crushed and separated into particles that were 0.1
178 – 1 mm in diameter. For the column experiments an intact drill core Kuru Grey granite column was
179 used.

180 2.3 Batch sorption experiments

181 The pH-dependent sorption of neptunium(V) on bentonite colloids was studied both in ambient air
182 and N₂ –atmosphere to investigate the influence of carbon dioxide on the neptunium(V) retention
183 and to simulate anoxic conditions in a final repository. Neptunium(V) sorption on crushed Kuru

184 Grey granite at constant neptunium(V) concentration of 10^{-6} M and granite concentration of 40 g/L
185 was investigated under ambient air atmosphere only, to simulate the experimental conditions of the
186 column experiments. The neptunium(V) concentration was kept constant at 10^{-6} M, the colloid
187 concentration ranged from 0.08 – 0.8 g/L, depending on the remaining colloid concentration in the
188 supernatant after centrifugation, as explained above (section 2.1). Isotherm studies were performed
189 under constant pH conditions (pH 8, 9, and 10) in N_2 -atmosphere as a function of neptunium(V)
190 concentration (10^{-10} to 5×10^{-6} M). TRIS and CHES buffers were used to achieve a constant pH in
191 the experiments. The final colloid concentrations for isotherm experiments at pH 8, 9, and 10 were
192 0.10, 0.06, and 0.18 g/L, respectively. 10 mM $NaClO_4$ was used as a background electrolyte
193 throughout the experiments. The sample pH was adjusted with 0.01–1 M NaOH and $HClO_4$
194 solutions. All samples were allowed to equilibrate under constant shaking for 7 days. Thereafter all
195 solid material including the colloids was separated by ultracentrifugation at 690000 g (90000 rpm)
196 allowing the determination of the non-sorbed neptunium(V) concentration from the supernatant.
197 The neptunium(V) concentration was determined by liquid scintillation counting (Quantulus) using
198 α/β – discrimination to separate out the β disintegrations from the Np-237 daughter nuclide Pa-233.

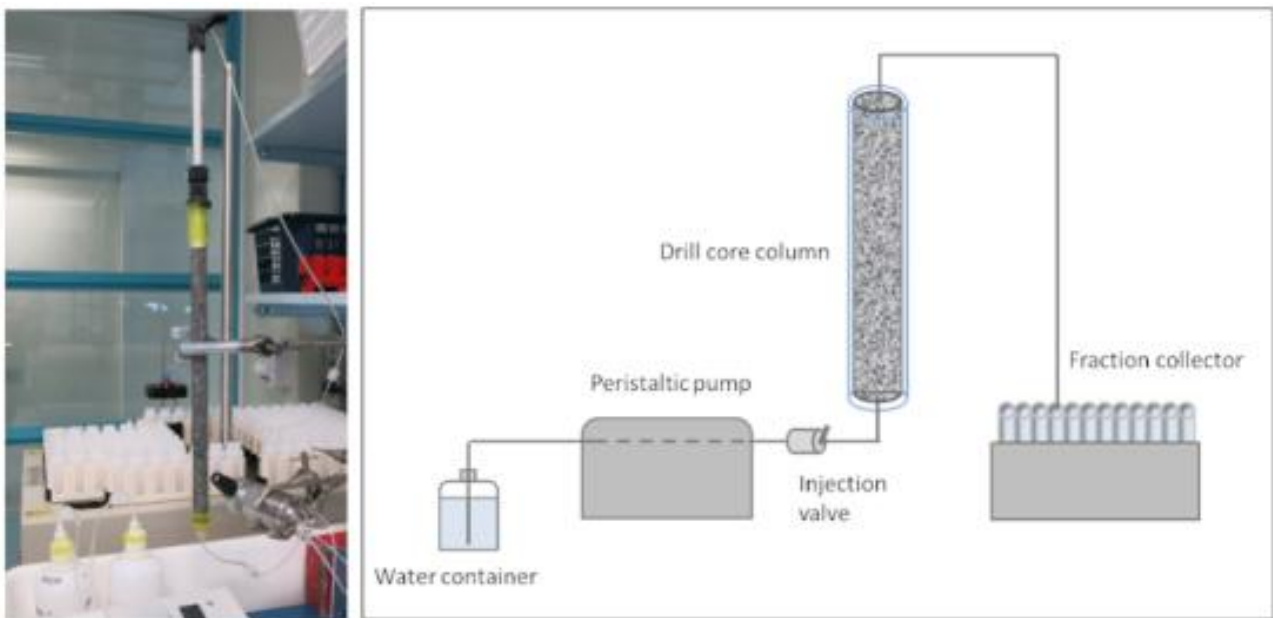
199 **2.4 Column experiments**

200 The effect of bentonite colloids on neptunium(V) migration was studied under flowing water
201 conditions in a drill core column, which has been used earlier in parallel with block-scale
202 experiments to evaluate the simplified radionuclide transport concept (Hölttä et al., 2008).

203 The intact drill core, 28 cm and 1.4 cm in diameter, was placed in the Glass Econo-Column[®] 30 cm
204 long and 1.5 cm in diameter, forming a flow channel in the 0.5 mm gap between the rod and tube.

205 The height of the column was adjusted with a Bio-Rad Flow Adaptor. Before the construction of the
206 column, the drill core was cleaned ultrasonically in ethanol to remove dust and any remnants from
207 the drilling procedure. The column experiments were performed under ambient air conditions. The
208 solution was continuously pumped through the column and the effluent was fed to a fraction

209 collector for determining the break-through of the tracer. The feed solution was replaced with the
210 colloid solution when experiments in the presence of colloids were conducted. Known volumes of
211 tracers were injected in the column through an injection loop with a volume of 12 μL . The total
212 volume of the flow channel in the column is 6.4 mL which is 500 times higher than the volume of
213 injection loop indicating that the tracer pulse is diluted after injection. Flow rates were controlled
214 with a peristaltic pump and determined by collecting and weighing several parallel fractions of the
215 background electrolyte that eluted through the columns in one hour. The experimental setup is
216 presented in Fig. 2.



217

218 Fig. 2. Experimental set-up and schematic design for the column experiments. The intact 28 cm
219 long drill core with a diameter of 1.4 cm was placed inside a column to form an artificial 0.5 mm
220 aperture flow channel between the core and the column walls.

221 Matrix diffusion and dispersion are the most important transport mechanisms for radionuclides in a
222 rock matrix (Moreno et al., 1997). Matrix diffusion can only be seen at very slow flow rates (Hölttä
223 et al., 1996, 2008). The flow rates of 0.3 mL/h and 0.8 mL/h for this study were selected based on a
224 previous study with the same drill core column (Hölttä et al., 2008). At the selected flow rates, the
225 transport of the conservative tracer is dominated by hydrodynamic dispersion caused by a

226 heterogeneous velocity field together with transverse molecular diffusion in the fracture. The
227 transverse diffusion in the fracture smooths out variable flow rates for different streamlines in the
228 circular slit around the core. The effects of matrix diffusion were shown in mobile iodine
229 breakthrough curves only at a very low flow rate of 0.04 mL/h, which excludes the possible
230 disturbing effects of the matrix in this study. The two different flow rates were chosen to elucidate
231 the effect of sorption kinetics on the breakthrough of neptunium(V). The flow field in the column
232 was characterized without colloids using a conservative tracer, chloride (Cl-36). The chloride
233 concentration in the injected tracer volume was 8.7×10^{-2} M, which quickly dilutes inside the
234 column. The total liquid volume in the first 0.5 cm of the column dilutes the injected tracer by a
235 factor of almost 10, which is below the ionic strength of 10 mM NaClO₄ used as background
236 electrolyte.

237 The experimental conditions in terms of pH were selected based on the results obtained in our
238 sorption experiments (see section 3.1). At pH 8, sorption of neptunium(V) on granite is low, and
239 increasing at pH 10. Thus, pH values of 8 and 10 were selected for the column experiments and 10
240 mM NaClO₄ was used as a background electrolyte to ensure comparable conditions to our previous
241 study (Elo et al., 2017) where we investigated neptunium(V) sorption on Na-montmorillonite
242 extracted from the MX-80 bentonite. The rock surfaces in the column were equilibrated by
243 continuously feeding 10 mM NaClO₄ through the column for several months up to one year. The
244 column was preconditioned at the wanted pH-values by feeding the background electrolyte through
245 the column for at least two weeks prior to experiments. The pH value from the collected solution
246 was determined before the experiment. Neptunium(V) transport through the granite columns was
247 monitored in the absence and presence of bentonite colloids. In both experiments, a rather high
248 neptunium(V) concentration of 2×10^{-4} M was chosen to assure that neptunium could be measured
249 from the collected fractions. However, due to dilution of neptunium(V) inside the column, a
250 concentration of 5×10^{-6} M (maximum concentration used in our isotherm experiments) is reached

251 already in the first 2 cm (out of 28 cm) in the column. In the experiments conducted in the presence
252 of bentonite colloids, the neptunium(V) tracer was injected into a constant and stable flow of
253 bentonite suspension with a colloid concentration ranging from 0.08 to 0.32 g/L. The eluted
254 neptunium(V)/colloid fraction was collected with a fraction collector and the neptunium(V)
255 concentration was determined from each fraction with LSC as explained above. Prior to the α/β -
256 counting, the colloid concentration in the solution eluted through the column was determined by
257 photon correlation spectroscopy (PCS) and the standard series presented in Fig. 1.

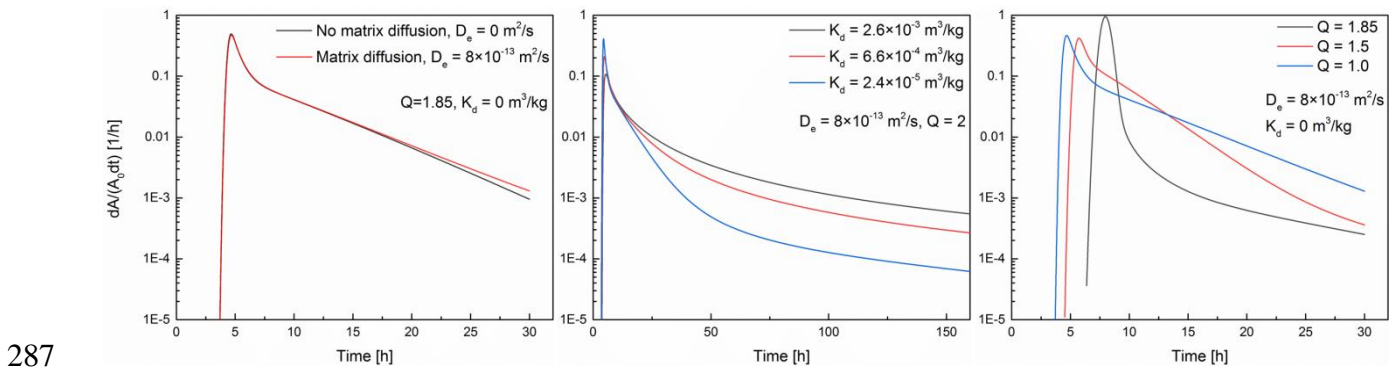
258

259 **2.5 Analytical modeling**

260 The breakthrough curves of the column experiments with chloride and neptunium(V) in the absence
261 and presence of MX-80 bentonite colloids were modeled using the analytical solution of advection–
262 matrix diffusion equation in cylindrical coordinates (see Kuva et al. 2016 for details). The analytical
263 solution for the problem was constructed using the methods reported previously (Kekäläinen et al.,
264 2011; Kekäläinen. 2014; Kuva et al., 2016). Recently, the model has been further developed so that
265 it is possible to take into account the channeled flow field (Voutilainen et al. 2018). The model
266 takes into account: (i) 1D diffusion in the flow field in direction of advection, (ii) 1D radial
267 diffusion in the rock matrix, (iii) sorption on mineral surfaces in the rock matrix, and (iv) the
268 channeled flow field between the cylindrical sample and the pipe surrounding the sample. The
269 analytical solution was derived for a Dirac delta function input starting from partial differential
270 equations describing the phenomena given above. The equations were solved by first writing them
271 in dimensionless form, finding the eigenvalues which are a combination of Bessel functions in the
272 cylindrical case, and solving the partial differential equations in Laplace space.

273 As a first step, the effect of the tubes before and after the granite column was subtracted from the
274 total flow-through time. Thereafter the flow velocity was scaled to get the raising part of the

275 breakthrough curve to the correct position. This was done by keeping the flow rate constant
 276 (measured value) and setting part of the water in stagnant state. Here, a scaling factor of 1 means no
 277 scaling and values greater than one mean that parts of the channel contains stagnant water (see Fig.
 278 3). Finally, the diffusion coefficient of chloride/neptunium(V) in water was adjusted to enable
 279 fitting of the late part of the breakthrough curve. The rock matrix did not affect the breakthrough
 280 curves of chloride and, thus, it could be used to characterize the flow field (see Fig. 3). In contrast,
 281 the matrix affected the breakthrough curves of neptunium(V) due to moderate sorption on granite.
 282 Thus, the K_d of neptunium(V) was adjusted to fit the late part of the breakthrough curves. In Fig. 3
 283 the influence of matrix diffusion (left), K_d (middle), and the stagnant-to- flowing water ratio (right)
 284 on the breakthrough curves are demonstrated. The values for porosity and the effective diffusion
 285 coefficient of Kuru Grey granite were selected according to previously determined values, i.e.
 286 0.47 % (Jokelainen et al. 2009) and $8 \times 10^{-13} \text{ m}^2/\text{s}$ (Ikonen et al. 2016), respectively.

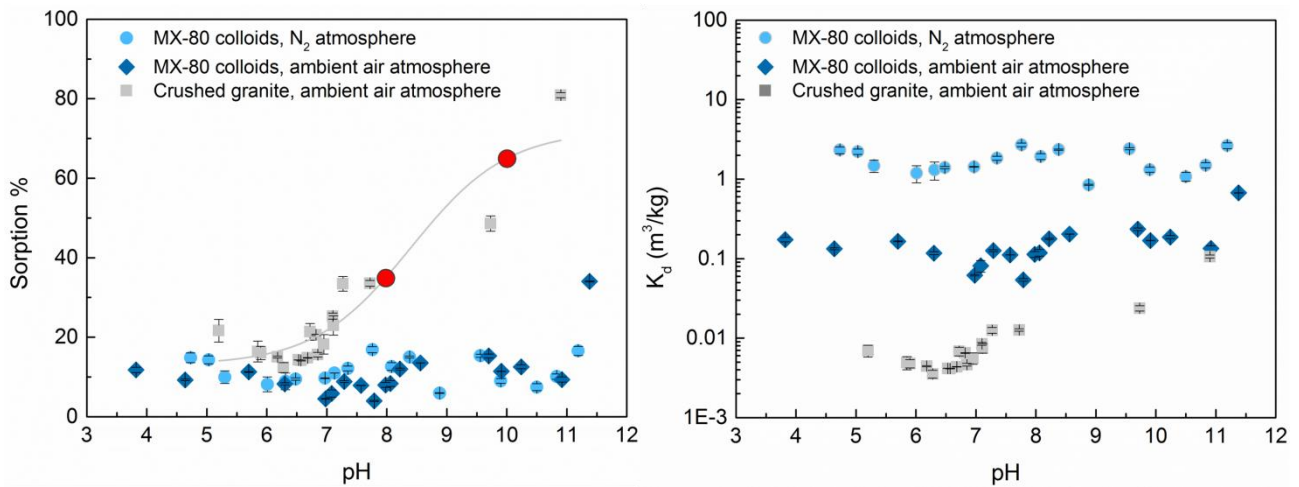


287
 288 Fig. 3 The influence of the effective diffusion coefficient (left), K_d (middle) and scaling of flow
 289 velocity (right) on the breakthrough curves.

290 3 RESULTS AND DISCUSSION

291 3.1 Batch sorption experiments

292 The pH-dependent sorption of neptunium(V) onto MX-80 bentonite colloids and crushed Kuru
293 Grey granite is presented in Fig. 4 as sorption percentages (left) and K_d values (right). Each data
294 point represents the average of duplicate measurements, and the error bars are standard deviations
295 of these measurements.



296
297 Fig 4. Neptunium(V) sorption on MX-80 colloids in N₂-atmosphere ($c_{\text{colloids}} = 0.08$ g/L), in ambient
298 air atmosphere (0.8 g/L), and on crushed Kuru Grey granite (40 g/L).

299 The neptunium(V) concentration was 10^{-6} M and background electrolyte 10 mM NaClO₄. The data
300 is given both as the sorption percentage vs. pH (left) and K_d vs. pH (right). For crushed granite, a
301 Boltzmann Fit of the sorption percentage vs. pH graph was made to select pH values (red spheres)
302 for the column experiments.

303 For neptunium(V) uptake by MX-80 bentonite colloids in N₂-atmosphere, the sorption percentage
304 remains almost stable up to a pH-value of 11.2 (16 %, $K_d = 2.6 \pm 0.2$ m³/kg). In addition, no clear
305 difference in the sorption percentage between N₂-atmosphere and ambient air atmosphere can be
306 seen except at pH 11.4 (34 %, $K_d = 0.671 \pm 0.003$ m³/kg). This implies that the formation of
307 neptunium(V)-carbonate complexes can be neglected at the chosen experimental conditions ($\text{pH} \leq$

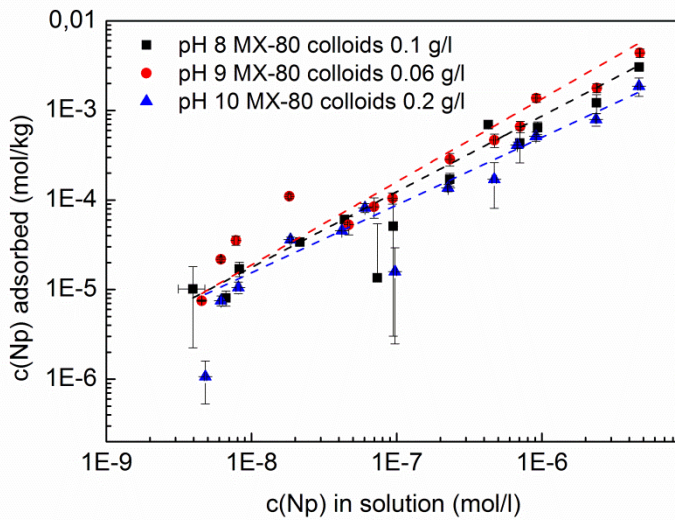
308 10) in the column experiments which, further, allows us to draw conclusions about the influence of
309 colloids on the neptunium(V) mobility in these experiments. A difference between N₂ and ambient
310 air atmosphere can be seen in the K_d values. This difference is constant over the whole pH-range
311 and cannot, therefore, be attributed to the presence of carbon dioxide which could result in
312 formation of soluble neptunium(V)-carbonate complexes in the neutral to alkaline pH-range. The
313 difference most likely arises from the absolute colloid concentration which is used in the calculation
314 of the K_d-value. As seen in Fig. 1, low colloid concentrations (below 1 g/L) are represented by only
315 one data point in the calibration curve. Therefore, a larger uncertainty is expected for the very low
316 colloid concentration range (such as the 0.08 g/L used in experiments conducted in N₂ atmosphere)
317 in comparison to 0.8 g/L (used at ambient conditions) and beyond. The constant sorption behavior
318 over the entire examined pH-range is not in agreement with our previous studies, investigating
319 neptunium(V) uptake by montmorillonite extracted and purified from MX-80 bentonite by B⁺Tech
320 and MX-80 bentonite colloids (Elo 2014, Elo et al. 2017). In those studies, a pH-dependent uptake
321 of neptunium(V) was found, which could be described by the presence of a small amount of ion
322 exchanged neptunium(V) in the acidic to circumneutral pH range and two surface complexes at pH-
323 values above 7. Also, the used solid/liquid -ratio was roughly 3.5 g/L which was the value at the
324 plateau where maximum neptunium(V) sorption was obtained. Furthermore, a K_d value of 2.6
325 (observed in the present study over the entire investigated pH-range) was obtained for
326 neptunium(V) sorption on montmorillonite only at pH-values exceeding 10. Both the pH-
327 independent behavior and the high K_d obtained in the present study for neptunium(V) sorption on
328 MX-80 bentonite colloids imply, that a large amount of neptunium is adsorbed on the colloids
329 through cation exchange on clay surfaces exhibiting permanent negative charge. This is in line with
330 the overall CEC (0.89 eq/kg), which can hold the overall amount of NpO₂⁺ cations present in the
331 clay suspensions, even for the lower colloid concentration of 0.08 g/L. The overall low sorption
332 percentage can be attributed to the low concentration of colloids used in the present study.

333 However, yet higher colloid concentrations are not expected in natural scenarios and would, thus,
334 not provide a realistic view of their influence on radionuclide mobility in the sub surface
335 environment. In fact, measured colloid concentrations at various underground laboratories such as
336 Äspö, Grimsel, and Gorleben, range from 10^{-6} g/L to some milligrams per liter (Degueldre et al.,
337 1988; Jansson, 2009; Laaksoharju and Wold, 2005; Smith and Degueldre, 1993). In the presence of
338 eroded bentonite, however, colloid concentrations of several hundred milligrams per liter (> 0.1
339 g/L) have been observed (Jansson, 2009; Missana et al., 2011). Thus, our sorption results for the
340 lower colloid concentration of 0.08 g/L can be expected to lie closest to the range expected in the
341 near-field of a future repository for spent nuclear fuel as a result of bentonite erosion.

342 Neptunium sorption on the crushed granite increases at pH 7 and above. The maximum sorption
343 percentage remains relatively low (81 %, $K_d = 0.106 \pm 0.005$ m³/kg at pH 11). Our results differ
344 somewhat from already published studies on neptunium(V) uptake by granite: Kumata and
345 Vandegraaf (1998), Kienzler et al. (2003), and Park et al. (2012) all found neptunium(V) reduction
346 to neptunium(IV) and a subsequent high retention of the reduced species on granite. Despite the
347 presence of amphibole, a mineral that often contains iron in the structure, in the Kuru Grey granite
348 used in the present study, no reduction of neptunium can be deduced from the low overall uptake in
349 the batch sorption studies and the high recovery of neptunium in the column experiments (discussed
350 later in the text).

351 Due to the pH-independent sorption of neptunium(V) on MX-80 bentonite colloids throughout the
352 investigated pH range, experimental conditions for the column experiments (discussed below in
353 section 3.2) were chosen based on the batch sorption data for crushed granite. Here, moderate
354 sorption of neptunium(V) was obtained in the circumneutral pH range with a slight increase of
355 sorption with increasing pH. Thus, pH values of 8 and 10 were selected for the column studies
356 based on the Boltzmann Fit of the sorption percentage vs. pH graph for crushed granite (see Fig. 4
357 left).

358 To investigate the neptunium(V) sorption behavior on MX-80 bentonite colloids at varying
 359 neptunium concentrations, which is of relevance in the column experiments where a neptunium(V)
 360 concentration gradient can be expected in the injection stage, sorption isotherms at constant pH, as a
 361 function of neptunium(V) concentration were conducted. Results are presented in Fig. 5. It can be
 362 seen that all three (pH 8, 9, and 10) curves are linear with a slope of 0.9 ± 0.12 , implying that close
 363 to ideal sorption conditions (characterized by a slope of 1) are maintained over the investigated
 364 concentration range.

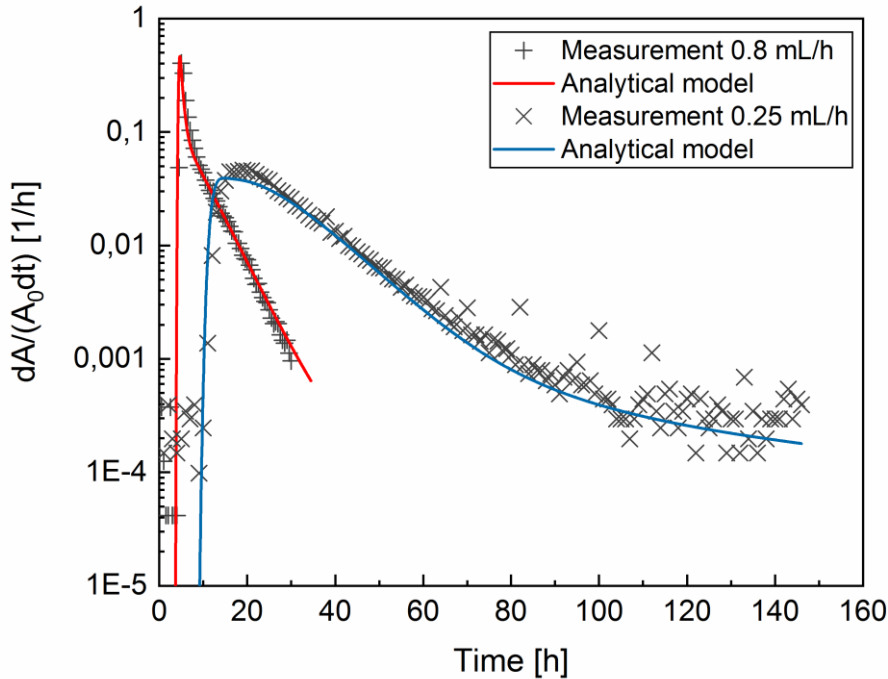


365
 366 Fig 5. Neptunium(V) sorption isotherms in N_2 -atmosphere on MX-80 colloids at pH 8 ($c_{\text{colloids}} = 0.1$
 367 g/L), pH 9 (0.06 g/L) and pH 10 (0.2 g/L). The neptunium(V) concentration is $10^{-9} - 5 \times 10^{-6}$.

368 3.2 Column experiments

369 3.2.1 Chloride (Cl-36)

370 The flow through properties of the drill core column were investigated by following the migration
 371 of a conservative chloride tracer through the columns at two different flow rates of 0.8 mL/h and
 372 0.25 mL/h (Fig. 6).



373

374 Fig. 6. Measured and modeled breakthrough curves of chloride in the absence of colloids through
 375 the drill core column. The chloride concentration in the injected tracer volume was 8.7×10^{-2} M. The
 376 recoveries of the Cl-36 tracer were approximately 100 %.

377

378 In Fig. 6 the breakthrough of chloride can be seen to be governed by the flow velocity. As expected,
 379 the breakthrough occurs earlier for the faster flow rate, followed by a slight tailing at both flow
 380 speeds, which can be attributed to dispersion in the column as previously shown by Park et al.
 381 (2012). The modeled breakthrough curves are in good agreement with the measured ones. The
 382 modeling results in terms of velocity scaling and diffusion coefficients for chloride in water are
 383 compiled in Table 1.

384 Table 1. The modeling results of measured breakthrough curves of chloride from the drill core
 385 column using different flow rates. The results include the velocity scaling and the self-diffusion
 386 coefficient of the element in water (D_0).

Element (pH)	Flow rate [mL/h]	Velocity scaling [-]	D_0 [m^2/s]
Cl-36 (8)	0.8	5	3×10^{-9}
Cl-36 (8)	0.25	2.5	3×10^{-9}

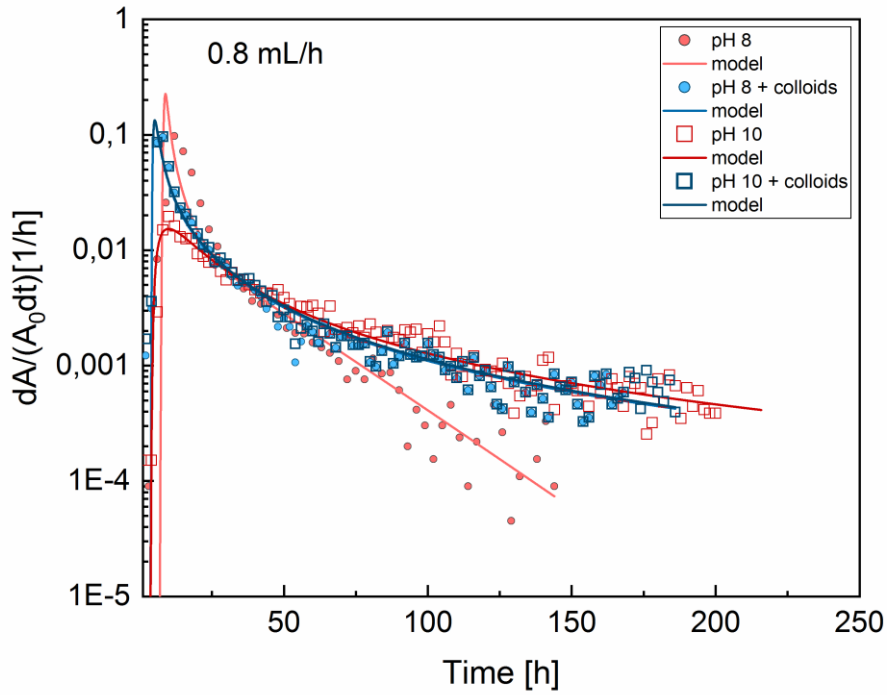
387

388 The velocity scaling can be seen to vary from one measurement to another. This may be due to a
389 slight displacement of the sample in the plastic tube resulting in a non-uniform aperture around the
390 sample. The variation in the aperture of flow channels has caused channeling of the flow field. A
391 direct consequence of the non-uniform aperture and the variations in the water flow, are the slightly
392 higher values obtained in the present study for diffusion coefficients for chloride in water in
393 comparison to the published value of $2.0 \times 10^{-9} m^2/s$ (Bastug and Kuyucak 2005). This compensates
394 the effect arising from a larger interaction between the flowing and stagnant water than with the
395 average aperture. However, the difference between the published and modeled diffusion
396 coefficients for chloride in water is minor when taking into account the robustness of the
397 experiment. In general, such channeling of the flow field is typical in natural systems and in
398 artificial systems for fracture flows.

399 3.2.2 Neptunium(V) and colloids

400 Neptunium(V) breakthrough curves for the flow rate of 0.8 mL/h in the absence (red symbols) and
401 presence (blue symbols) of bentonite colloids in the drill core granite column experiments at pH 8
402 and 10 are presented in Fig 7. Results obtained for the flow rate of 0.3 mL/h are presented in Fig. 8.

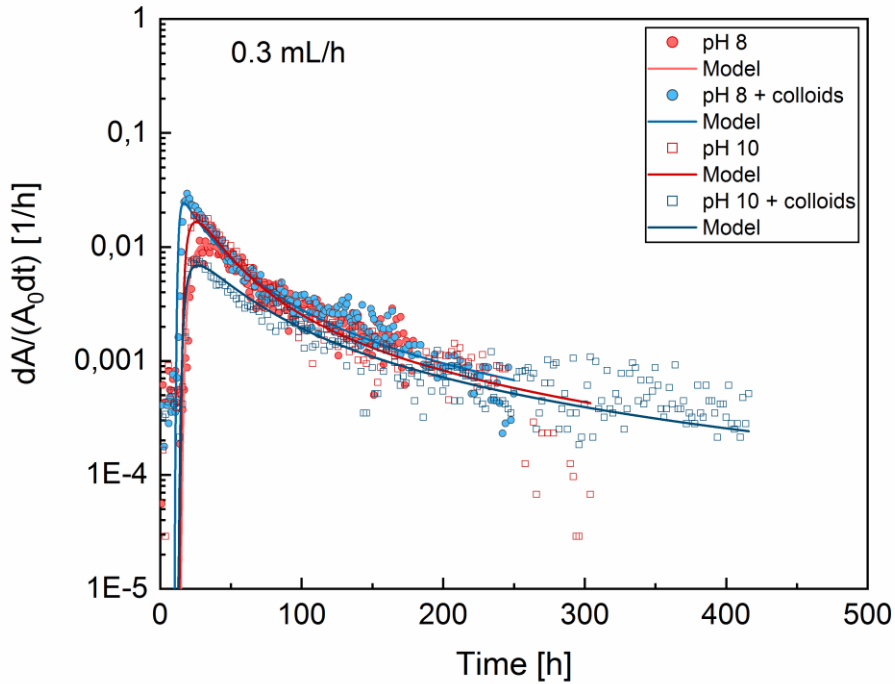
403



404

405 Fig 7. Measured and modeled breakthrough curves for neptunium(V) through the drill core column
 406 at a flow rate of 0.8 mL/h in 10 mM NaClO₄, pH 8 (closed symbols) and pH 10 (open symbols) in
 407 the absence (red traces) and presence of colloids (blue traces). The neptunium(V) recoveries at pH 8
 408 and pH 10 were 95% and 68 %, respectively, in the absence of colloids. In the presence of colloids
 409 recoveries of 99% (pH 8) and 98% (pH 10) were obtained.

410

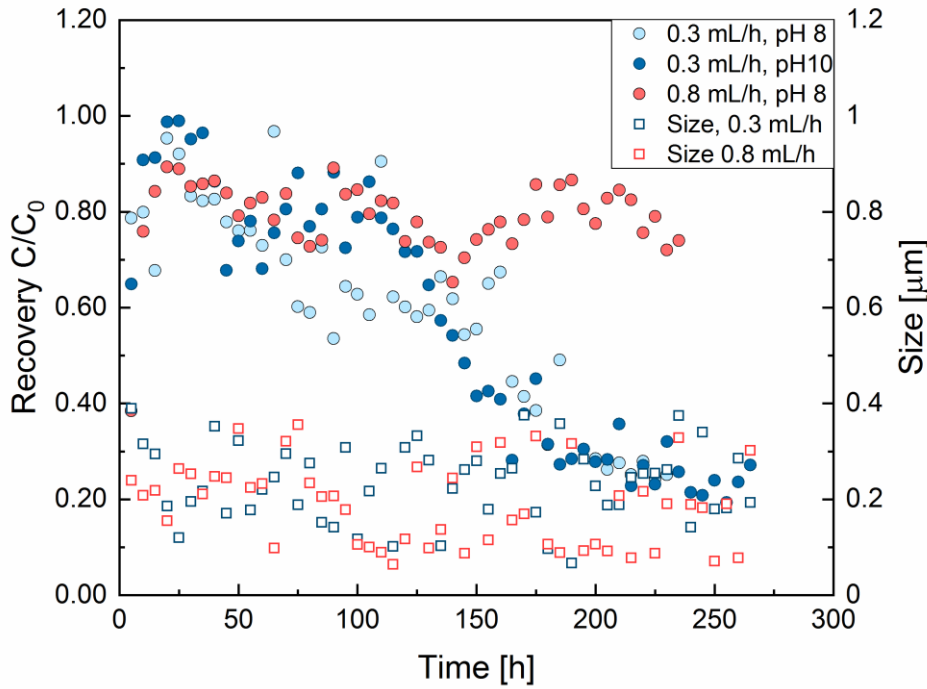


411

412 Fig 8. Measured and modeled breakthrough curves for neptunium(V) through the drill core column,
 413 flow rates of 0.3 mL/h in 10 mM NaClO₄ pH 8 (closed symbols) and 10 (open symbols) in the
 414 absence (red traces) and presence of colloids (blue traces). The neptunium(V) recoveries at pH 8
 415 and pH 10 were 96% and 92 %, respectively, in the absence of colloids. In the presence of colloids
 416 recoveries of 100% (pH 8) and 60% (pH 10) were obtained.

417 Breakthrough curves for the colloids are presented in Fig. 9. Here, only the results obtained for the
 418 flow rate of 0.3 mL/h at pH 8 have been collected together with the neptunium(V) data presented
 419 above, by determining the mean particle size and derived count rate with PCS from all collected
 420 fractions. The colloid breakthrough curves for the experiments at 0.8 mL/h, pH 8 and 0.3 mL/h, pH
 421 10 are results of separate experiments. The colloid concentrations in these experiments were 0.25
 422 g/L and 0.32 g/L, respectively. For the flow rate 0.8 mL/h, the recoveries of colloids were 80 ± 9 %
 423 during the whole experiment. For the flow rate of 0.3 mL/h, the recoveries fluctuated between 65 %
 424 and 98 % in the beginning and thereafter decreased down to 20 % suggesting filtration of colloids
 425 into the stagnant areas of the flow channel or tubing. The mean particle sizes stayed constant at 190

426 ± 99 nm (0.8 mL/h) and 220 ± 85 nm (0.3 mL/h) over the whole collection time, which is in line
427 with the results obtained in our colloid stability tests where a constant colloid size of 215 ± 54 nm
428 was maintained over 30 days (720 hours).



429
430 Fig. 9. The breakthrough and mean particle size of colloids. The colloid breakthrough at 0.3 mL/h,
431 pH 8 (light blue spheres, 0.08 g/l) was determined from the neptunium(V) experiment in the
432 presence of colloids. The breakthrough at 0.3 mL/h, pH 10 (0.32 g/l) and 0.8 mL/h, pH 8 (0.25 g/l)
433 (blue and red spheres) as well as mean particle sizes (squares) are determined from separate colloid
434 breakthrough experiments.

435 3.2.3 Discussion

436 The modeled neptunium(V) breakthrough curves in the absence and presence of colloids are in
437 good agreement with the measured ones. The modeling results in terms of velocity scaling and
438 diffusion coefficients for neptunium in water are compiled in Table 2.

439 Table 2. The neptunium(V) recoveries and modeling results of measured breakthrough curves from
 440 the drill core column using different flow rates. The modeling results include the velocity scaling
 441 and the sorption distribution coefficient (K_d). The self-diffusion coefficient of the element in water
 442 (D_0) was $3 \times 10^{-9} \text{ m}^2/\text{s}$ in all cases.

Element (pH)	Flow rate [mL/h]	velocity scaling [-]	K_d [m^3/kg]	Np-237 recovery [%]
Np-237 (8)	0.8	1	8×10^{-5}	95
Np-237 + col (8)	0.8	2	0.003	99
Np-237 (10)	0.8	2	0.004	68
Np-237 + col (10)	0.8	2	0.003	98
Np-237 (8)	0.3	1.5	0.0009	96
Np-237 + col (8)	0.3	2	0.0005	100
Np-237 (10)	0.3	1.5	0.001	92
Np-237 + col (10)	0.3	1.7	0.002	60

443

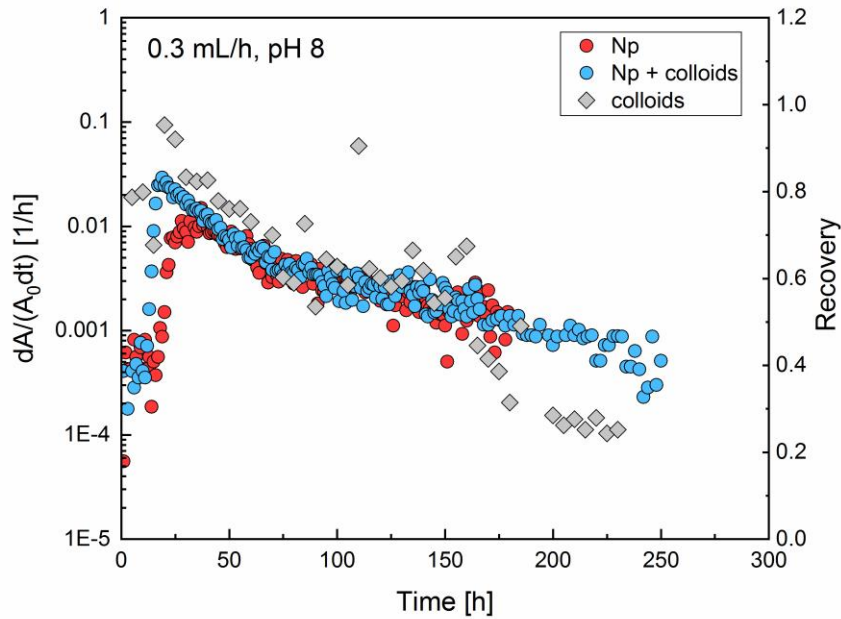
444 The observed rapid increase of the breakthrough curves obtained for the intact drill core column are
 445 mainly governed by the ratio between stagnant and flowing water in the columns. In the
 446 experiments conducted at the slower flow rate (Fig. 8), the pre-peak position remains constant in the
 447 presence and absence of colloids, while a shift can be seen for the 0.8 mL/h data. The observed
 448 differences in this pre-peak position must, thus, originate from slight differences of the drill core
 449 position in the plastic tubes during the breakthrough experiments. The modeled breakthrough
 450 curves (Figs. 7 and 8) show that the flow field is channeled in the neptunium(V) experiments and
 451 that typically about half of the flow channel has flowing water (see Table 2). The raise of the
 452 breakthrough curve is not as steep as for chloride. This demonstrates that the flow field cannot be
 453 fully modeled with the simple dual flow velocity model as the sorbing nuclide interaction with the

454 rock matrix is stronger than such models predicts. However, in this case the late part of the
455 breakthrough curve cannot be explained by only matrix diffusion into stagnant water and later back
456 to the flowing area and, thus, sorption affects the late part of the breakthrough curve.

457 A higher tail of the breakthrough curves, especially at the flow velocity of 0.8 mL/h, can be seen
458 with increasing pH in the absence of colloids, indicating that neptunium(V) sorbs on the granite
459 surface as also observed in our batch sorption studies on the crushed material (Fig. 4). This can also
460 be seen from the K_d values determined by the modeling (Table 2). Here, the K_d values for
461 neptunium(V) without colloids vary from $8 \times 10^{-5} \text{ m}^3/\text{kg}$ to $0.004 \text{ m}^3/\text{kg}$. These values are between
462 10-200 times lower than obtained in our batch sorption experiments ($\sim 0.015\text{-}0.030 \text{ m}^3/\text{kg}$, pH =8-
463 10). Such a large discrepancy could be a result of a much smaller specific surface area of the
464 column material in comparison to the crushed granite material used in the batch sorption
465 experiments. In Hölttä et al. (1997), a specific surface area of $0.05\text{-}0.07 \text{ m}^2/\text{g}$ and $1.2 \text{ m}^2/\text{g}$ for intact
466 and crushed tonalitic rock, respectively, has been reported, i.e. a difference of a factor of
467 approximately 20. Other factors such as a slow sorption kinetic for neptunium(V) uptake by granite,
468 as shown in Park et al. (2012) could play a role in addition to a high reversibility of neptunium(V)
469 sorption under flowing water conditions as was shown for neptunium(V) uptake by montmorillonite
470 in our previous study (Elo et al. 2017). Slow sorption kinetics is supported by the results obtained at
471 pH = 8, where more than 10 times higher sorption distribution coefficient is obtained for the 0.3
472 mL/h flow rate in comparison to the 0.8 mL/h one. This is well in agreement with the overall
473 neptunium(V) column residence time, which was approximately 4 days for 0.3 mL/h and only 25
474 hours for the 0.8 mL/h experiment, whereas the equilibration time for batch sorption studies was 7
475 days. The residence time is taken as the time between tracer injection and elution through the
476 column. At pH = 10 the sorption distribution coefficient is of the same order of magnitude for both
477 flow rates. Whether this is an effect of the stagnant vs. flowing water volume which is
478 systematically higher for the larger flow rate (see tables 1 and 2) or due to changes in the surface

479 complexation mode (e.g. larger amount of inner-sphere sorption at pH = 10), we cannot deduce
480 based on available data. Thus, for a proper assessment of the underlying reasons between
481 differences in neptunium(V) uptake under stagnant vs. flowing water conditions, detailed
482 understanding of sorption kinetics, reversibility of the sorption reaction, and knowledge of the
483 complexation mechanism on the solid surface are required.

484 The presence of colloids has almost no influence on the neptunium(V) breakthrough at the slower
485 flow rate of 0.3 mL/h and at the higher pH for the 0.8 mL/h flow rate. Based on our batch sorption
486 data, a constant uptake of neptunium(V) of around 10% of the total neptunium(V) concentration is
487 expected by the bentonite colloids at pH = 8 and 10. In the granite column the sorption percentage
488 is more difficult to assess, as the solid to liquid ratio is unknown. However, a larger amount of
489 neptunium(V) sorption is expected at pH = 10 on the column material, implying that a potential
490 influence of the colloids should be more pronounced at this pH-value. Such an influence, however,
491 is not seen in our column studies. At 0.3 mL/h flow rate, almost no retention of neptunium(V) can
492 be seen on the column material both in the presence and absence of colloids. Therefore, it is
493 difficult to assess if the eluted neptunium(V) in the presence of colloids is associated with the
494 colloids or migrating with the flowing water. The colloid breakthrough behavior at this flow
495 velocity seems to oscillate between 60 and 100 % recoveries before it decreases toward 20%. As
496 already briefly mentioned, this decrease of the colloid breakthrough is most likely a result of
497 filtration of colloids into the stagnant areas of the flow channel or tubing. A similar oscillating
498 breakthrough of neptunium(V) is not observed, which would imply that at least the majority of
499 neptunium(V) is eluted from the column in the aqueous phase. A slight indication for colloid-borne
500 neptunium(V), however, is visible after approximately 160 hours (Fig. 10) when comparing the
501 breakthrough behavior of neptunium(V) with that of the colloids. The abrupt decrease of colloid
502 breakthrough (gray symbols) at this time point is associated with a small kink in the neptunium(V)
503 breakthrough curve (light blue symbols).



504

505 Fig. 10. Comparison between the breakthrough behavior of neptunium(V) (red and light blue
 506 symbols), and the breakthrough (gray symbols) and mean particle sizes (dark blue symbols) of
 507 colloids at the flow velocity of 0.3 mL/h and pH = 8.

508

509 At pH 10, both flow rates show a small difference in the sorption distribution coefficient in the
 510 presence of colloids. The difference, however, is not systematic, i.e. a slightly lower K_d value is
 511 obtained at 0.8 mL/h while the opposite is true at 0.3 mL/h in the presence of bentonite colloids.
 512 Therefore, this difference can most likely be attributed to the experimental error in the column
 513 investigations and their modeling rather than to an actual effect caused by the colloids. The
 514 situation, however, is very different at pH = 8 for the faster flow rate, where a steeper tailing of the
 515 breakthrough curve can be seen in the absence of colloids (Figure 7), implying that a higher
 516 retention of neptunium(V) in the column occurs in the presence of colloids. This is also supported
 517 by the modeled K_d values which are larger in the presence of colloids than in the absence of them
 518 by a factor of almost 40. As there is almost no retention to be seen on the granite in the absence of
 519 colloids, the enhanced uptake by the colloids could be related to the adsorption of colloids on the

520 column material, providing further sorption sites for neptunium(V) attachment inside the column.
521 Alternatively, colloids may interrupt the flow path, reducing the accessible flow channels for
522 neptunium(V) and therefore influence the breakthrough properties of neptunium(V). Such a
523 clogging phenomenon of colloids was observed by Missana et al (2008). When looking at the
524 colloid breakthrough curve at this flow velocity and pH, a similar oscillating behavior can be seen
525 as for the lower flow velocity of 0.3 mL/h. However, the recovery never reaches 100 % (oscillation
526 occurs between 70 and 90 %) and there is no decrease of the colloid recovery as observed for the
527 slower flow velocity. Thus, a clogging phenomenon cannot be confirmed based on the colloid
528 breakthrough data and we must explore the possibility of colloid attachment on the column material
529 resulting in the retention of colloid-borne neptunium(V) in the column. The point of zero charge or
530 isoelectric point of granite has been reported to lie around pH 8 – 9 (Charalambos P., 2001; Chen T.
531 et al., 2013). The IEP for bentonite colloids is much lower. In fact, we measured a constant negative
532 charge of montmorillonite over the entire examined pH-range of 3-11 (Elo et al., 2017). At pH 8
533 some of the surface groups on granite still carry a positive charge, thus, enabling the electrostatic
534 attachment of colloids on the surface. At pH 10 such electrostatic attachment will be decreased due
535 to the larger amount of negatively charged surface groups. However, if pH-dependent colloid
536 attachment on granite occurs, the effect should be visible also at pH 8, which is not the case in our
537 column experiments. Thus, a definite conclusion of the underlying reasons for the decreased
538 breakthrough of neptunium(V) in the presence of colloids at pH 8 and the flow velocity of 0.8 mL/h
539 cannot be given.

540

541 4 CONCLUSIONS

542 In this study, we investigated the influence of MX-80 bentonite colloids on neptunium(V) migration
543 in granite media. Neptunium(V) uptake by crushed granite was found to be pH-dependent, whereas
544 neptunium(V) uptake by MX-80 bentonite colloids was pH-independent, unlike observed for
545 montmorillonite purified from the MX-80 bentonite. The column experiments under flowing water
546 conditions were conducted for chloride as a non-sorbing tracer and for neptunium(V) at two pH
547 values (pH = 8 and 10) and two flow rates (0.3 mL/h and 0.8 mL/h). The resulting breakthrough
548 curves were thereafter modeled using the analytical solution of advection–matrix diffusion equation
549 in cylindrical coordinates. The modeling results of chloride breakthrough curves indicated that the
550 flow field consisted of flowing and stagnant water and that tail of the breakthrough curve was
551 caused by matrix diffusion into the stagnant water and later back into flowing water. The modeling
552 results for neptunium(V) breakthrough curves were in good agreement with the experimental
553 results. A tailing of neptunium(V) breakthrough curves in comparison to the conservative tracer was
554 observed, which could be explained by a higher retardation of neptunium(V) in the column caused
555 by sorption on the granite. The sorption was in general lower at pH 8 than at pH 10. In addition, the
556 tailing was almost identical in the absence and presence of MX-80 bentonite colloids, implying that
557 the influence of colloids on the neptunium(V) mobility is almost negligible. With respect to
558 conditions in the repository environment where pH ranges from circumneutral to slightly alkaline,
559 and the groundwater is mildly oxic e.g. due to the glacial melt waters, the migration of
560 neptunium(V) is favored due to low sorption onto granite media. Therefore, at low flow rates matrix
561 diffusion becomes an important process retarding neptunium migration under oxic conditions.

562

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