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1 **Montmorillonite colloids. I: Characterization and stability of dispersions**

2 **with different size fractions**

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11 **Abstract**

12 Bentonite is planned to be used as a technical barrier in the final storage of spent nuclear fuel
13 and high level vitrified waste. In contact with ground water of low ionic strength,
14 montmorillonite colloids may be released from the bentonite buffer and thereby enhance the
15 transport of radionuclides (RNs) sorbed. In the present case, clay colloids represent
16 aggregates of several clay mineral layers. It is of major importance to determine RN sorption
17 properties for different sizes of montmorillonite aggregates, since size fractionation may
18 occur during particle transport in natural media. In this study, a protocol for size fractionation
19 of clay aggregates is developed, by sequential and direct centrifugation, in presence and
20 absence of organic matter. Seven colloidal fractions of different mean aggregate sizes are
21 obtained ranging, when considering the mean equivalent hydrodynamic sphere diameter
22 (ESD), from ~960 nm down to ~85 nm. Applying mathematical treatments (Jennings and
23 Parslow, 1988) and approximating the clay aggregates to regular disc-shaped stacks of clay
24 mineral sheets, results in mean surface diameters varying from ~1.5 μm down to ~190 nm.
25 All these colloidal fractions are characterized by XRD, IC and ICP-OES where they are found

26 to have the same chemical composition. The number of edge sites (aluminol and silanol) is
27 estimated (in mol/kg) for each colloidal fraction according to (Tournassat et al., 2003). It is
28 calculated from the mean particle sizes obtained from AsFIFFF and PCS measurements,
29 where the clay aggregates are approximated to regular disc-shaped stacks of clay mineral
30 sheets. The estimated number of edge sites varies significantly for the different clay
31 dispersions. In addition, stability studies using the various clay colloidal fractions are
32 performed by addition of NaCl, CaCl₂ or MgCl₂, in presence or absence of organic matter,
33 where no difference in stability is found.

34 **Keywords**

35 Montmorillonite colloids, characterization, size separation, number of edge sites, nuclear
36 waste disposal, colloidal stability

37 **1 Introduction**

38 In Swedish and Finnish repository designs (SKB, 2010; Vieno and Ikonen, 2005), high level
39 nuclear waste is foreseen to be placed in massive metal canisters, surrounded by a large
40 volume of natural or compacted bentonite as a barrier. The functionality of the clay is
41 primarily to stabilize the canister in case of movements in the bedrock and to seal small
42 fractures in the vicinity of the canister. The barrier is planned to prevent corrosive elements
43 from the surrounding, such as sulfide, thiosulfate and polythionates (Macdonald and Sharifi-
44 Asl, 2011) to come in contact with the canister. In case of canister failure, the barrier should
45 retard radionuclides (RNs) present in the spent nuclear fuel to be transported through the
46 geosphere towards the biosphere. Due to its high swelling pressure, cation exchange capacity
47 and retention properties, bentonite has an excellent buffer capacity (Karnland et al., 2006).
48 The main mineral component in bentonite is montmorillonite, an Al-rich smectite. Smectites
49 are intrinsically small particles, whereby they can be of colloidal sizes (i.e. particles of 1 nm -

50 1 μm in at least one dimension in dispersion (Stumm, 1993)). In this work, the term clay
51 colloids refer to aggregates, consisting of stacks of several clay mineral layers.

52 Over the estimated lifetime of the storage (i.e. 1 million years) in northern countries such as
53 Sweden and Finland (SKB, 2010), cycles of glaciations can be expected. In the worst case
54 scenario expected in Sweden, a large amount of glacial melt water will be transported through
55 fractures in the bedrock, down to repository depth and displace the old ground water that has
56 equilibrated with mineral surfaces for a very long time. Glacial melt water has a chemical
57 composition with low ionic strength, different from the original porewater. The chemical
58 composition of future glacial melt water is assumed to be similar to glacial melt waters of
59 today. It can be simulated by water types of pH 8-9 and low ionic strength, i.e. $5 \cdot 10^{-4}$ M in the
60 worst case scenario cited above (Brown, 2002). The montmorillonite colloid stability is
61 known to increase with decreasing ionic strength, as demonstrated in several laboratories and
62 field experiments studies over a few months' timeframe (Geckeis et al., 2004; Missana et al.,
63 2003; Schäfer et al., 2012) and can also be calculated from the DVLO-theory (Liu et al.,
64 2008). In contact with glacial melt water, the bentonite barrier may release montmorillonite
65 colloids that can be transported away from the barrier through the geosphere. In case of large
66 mass loss, the buffer functionality will be endangered. Also, in the case of a canister failure,
67 the transport of RNs can be enhanced, when transported by mobile montmorillonite colloids
68 (Möri et al., 2003).

69 Physically, colloid mobility depends strongly on the geometry of the fractures in the bedrock,
70 where fracture size distribution, surface roughness and surface charge are the most important
71 characteristics (Darbha et al., 2010; Filby et al., 2008). Chemically, the colloid mobility is
72 influenced by the mineral composition of the fracture filling material (FFM) and the pore
73 water matrix. The colloid mobility is also dependent on physical and chemical properties of
74 the clay aggregates themselves, i.e. the size heterogeneity, mineral composition and surface

75 charge. The physical and chemical properties of the bedrock are specific for each fracture,
76 though in general a separation of particles according to their size during transport is expected
77 in most systems. In a clean fracture system, i.e. fractures with low amount of FFM, and with a
78 high water velocity, a laminar flow is expected and transport of all colloid sizes is expected
79 more or less equally due to their ability to be transported with the water flow (Huber et al.,
80 2012). In contrary, if the fracture contains a larger amount of FFM, it will act as a porous
81 material, where the larger particles can be transported faster as a result of size exclusion
82 effects, sticking, clogging etc. Due to the possible particle size separation in bedrock
83 fractures, the size of the montmorillonite aggregates produced and their stability are important
84 parameters for RN transport. The thermodynamic and kinetic strength of RN-colloid
85 interaction determine the potential flux of radiotoxic waste components through the
86 geosphere. In fact, those RNs being weakly bound to colloids or showing a relatively fast
87 desorption from colloids will most likely not be carried by the montmorillonite colloids but
88 will be sorbed by the mineral surfaces instead (Huber et al., 2014).

89 Simplified models of RN and clay colloid transport are currently used in safety assessments
90 for estimating the RN transport, but presently they do not take into consideration the size
91 heterogeneity of the clay aggregates (Vahlund and Hermansson, 2006). Consequently, one
92 may wonder whether normalized sorption coefficients (K_D) for RNs are valid expressions for
93 quantifying RN-montmorillonite interactions, since the ratio is given for a mean particle size
94 distribution and do not take into account polydispersity. An alternative, and perhaps better,
95 expression for quantifying the sorption capacities of surface complexed RNs is to take into
96 consideration the amount of edge sites in the colloidal dispersions. With this treatment,
97 eventual size dependent differences will be taken into account. This is valid as long as the
98 smaller particles are miniatures of the larger clay mineral particles, which may not be the case
99 for nanosized particles (Bergaya et al., 2006). Note that this approach is not adapted for RNs

100 sorbing by cation exchange (i.e. Cs^+ , Sr^+ etc.). Large differences in surface structure between
101 larger and smaller clay particles may also be reflected in macroscopic properties, such as
102 colloidal stability (Bessho and Degueldre, 2009). In modeling, transport of RNs may be
103 under- or overestimated (Wold, 2010), e.g. the K_D -values are not accurate if only the smaller
104 aggregates are transported and not the larger ones, or vice versa. Normalizing sorption
105 capacity to the number of edge sites might improve transport calculations of RNs sorbed to
106 different clay aggregate sizes. Furthermore, this treatment of K_D -values could be implemented
107 to other systems, such as metal complexation to particles and their retardation in soils, as well
108 as colloidal transport in soil and surface waters (Gao et al., 1997; Lee et al., 2001; Nakamaru
109 and Uchida, 2008; Oliver et al., 2006). In addition to questionable normalization of sorption,
110 i.e. K_D -values in transport modelling, there is a lack of sorption and desorption kinetic data
111 for RNs onto different size fractions of montmorillonite aggregates which should be
112 implemented for improved safety assessments calculations (Wold, 2010).

113 The aim of this work is to develop a method to separate montmorillonite aggregates into
114 defined size fractions, to characterize these fractions and finally to determine if the mean clay
115 aggregate size has any influence on the colloidal stability of montmorillonite. We describe the
116 protocol used to obtain different size fractions, a protocol which may be applied to any type of
117 clay dispersions. In addition, characterization of the different clay aggregate fractions such as
118 mean size, concentration, and the chemical composition of the colloidal dispersions is
119 presented. Furthermore, we describe stability studies performed on the colloidal fractions in
120 order to investigate the influence of ions which can be present in glacial melt water (Na^+ ,
121 Ca^{2+} , Mg^{2+} (Missana et al., 2003)) or degraded organic matter (Bhatia et al., 2010). In
122 separate studies (Norrfors et al., 2015), we investigate the RNs sorption/desorption behavior
123 in presence of these clay aggregate size fractions.

124 **2 Material and Methods**

125 *2.1 Clay, organic matter, chemicals, synthetic ground water*

126 All samples are prepared with ultra-pure water (Milli-Q system, 18.2 MΩ/cm resistivity) and
127 chemicals of reagent grade. The source of silicon was a standard solution of Si in H₂O (1000
128 mg/L, Spex Certiprep). The Wyoming MX-80 bentonite from American Colloid Co. is used
129 as starting material for all experiments without any pretreatment. The MX-80 contains
130 approximately 82% montmorillonite with the structural formula:
131 $\text{Na}_{0.30}(\text{Al}_{1.55}\text{Fe}_{0.21}\text{Mg}_{0.24})(\text{Si}_{13.96}\text{Al}_{0.04})\text{O}_{10}(\text{OH})_2$, $M_w = 372.6$ g/mol (Karnland et al., 2006) and
132 has a cation exchange capacity (CEC) of approximately 0.75 meq/g (measured according to
133 (Meier and Kahr, 1999)).

134 The fulvic acid (FA-573) used as organic matter in this study was extracted from a natural
135 ground water (Gohy573) originating from the Gorleben site, Germany (Wolf et al., 2004) and
136 subsequently purified and characterized. A detailed description can be found in (Wolf et al.,
137 2004). The elemental composition of the FA used in this work is as follows (Wolf et al.,
138 2004): C: (54.1 ± 0.1) %, H: (4.23 ± 0.08) %, O: (38.94 ± 0.04) %, N: (1.38 ± 0.02) % and S:
139 (1.32 ± 0.01) %. The proton exchange capacity is 6.82 ± 0.04 meq/g. In this study, a small
140 amount of FA is weighted, dispersed in NaOH and diluted in the corresponding initial clay
141 stock dispersions as described below. The dissolved organic carbon content is measured with
142 a TOC analyser (TOC-5000, Shimadzu).

143 A synthetic carbonated ground water (SGW) is prepared in order to simulate a glacial melt
144 water of low ionic strength. In the present case, we tend to the composition of the granitic
145 groundwater coming from the Grimsel Test Site (Geckeis et al., 2004; Möri et al., 2003). This
146 is done by mixing the requested amounts of the different salts (NaOH, NaCl, CaCl₂, MgCl₂,
147 NaF, Na₂SO₄ and NaHCO₃) and an aliquot of the Si standard solution in ultra-pure water. The
148 final composition of the SGW is the following: Na⁺ (28.4 mg/L, 1.2 mM), Ca²⁺ (1.49 mg/L,
149 0.05 mM), F⁻ (2.8 mg/L, 0.1 mM), Cl⁻ (2.64 mg/L, 0.074 mM), SO₄²⁻ (4.13 mg/L, 0.04 mM),

150 Si (0.014 mg/L, 0.5 μ M) and HCO_3^- (84 mg/L, 1.4 mM). The ionic strength is below $2 \cdot 10^{-3}$ M
151 and the pH is 8.4 ± 0.1 .

152

153 *2.2 Fractionation by sequential and direct (ultra-)centrifugation*

154 50 g of unpurified MX-80 bentonite is added to 5 L SGW (10 g clay/L). The dispersion is
155 regularly stirred during one day and then let to settle during three days in order to remove the
156 larger clay fractions and accessory mineral phases. After sedimentation the top 4 L are
157 isolated. It constitutes the colloidal dispersion S0. The residual solid phase (named R0) is
158 stored for further studies (Figure S1 in the supporting information file 1 (SIF-1)). Sequential
159 centrifugation (Thermo Scientific Centrifuge 2.0, with 50 mL PE centrifugation tubes, VWR,
160 Germany) or ultra-centrifugation (Beckmann Ultracentrifuge, XL90, with 100 mL Quick-seal
161 centrifuge tubes, Beckmann) is then performed at increasing speeds and times to obtain
162 various clay colloidal dispersions, starting from the supernatant S0 similarly to the protocol
163 presented in (Perret et al., 1994). The resulting supernatant after the first centrifugation step
164 corresponds to the colloidal dispersion S1 and the corresponding solid residual, R1.
165 Thereafter, the sequential centrifugation is repeated three times, where the last centrifugation
166 step is an ultra-centrifugation, leading to the supernatant S3.5. A schematic diagram for the
167 fractionation protocol is presented in the supporting information file 1, SIF-1, Figure S2. The
168 corresponding centrifugation times and speeds are summarized in Table 1. Higher
169 centrifugation speeds (up to 235 000 g) and filtrations (see SIF-2) are tested but result in
170 removing a too large part of the clay particles. Consequently, only the fractions S0 to S3.5 are
171 used in the present work.

172 In addition to the sequential centrifugation, and for comparison, two supernatants (noted with
173 the prefix UC and UC, FA) are collected directly from the supernatant S0 after only one ultra-
174 centrifugation step, using the same speed and time as the ones used to obtain the dispersion

175 S3.5. For that purpose, an initial supernatant S0 is collected after 1 day stirring and 3 days
 176 sedimentation as described above, in presence (UC, FA) or absence (UC) of 11.8 mg/L FA.

177 Finally, the truly dissolved concentrations of Si, Al, Ca, Mg and Fe in equilibrium with clay
 178 minerals are those determined after the strongest centrifugation step (1h at 235 000 g, SIF-2).
 179 To determine the amount of each element in the clay particles, the truly dissolved
 180 concentration is subtracted from the total concentration measured in the dispersion.

181

182 **Table 1: Conditions for fractionation of the clay dispersions, and clay aggregate sizes expected in the**
 183 **residuals (R_i) and in the supernatants (S_i).**

Dispersion	Conditions of separation (C: centrifugation; UC: ultracentrifugation)	Size expected in the ith residual clay fraction (R_i) in nm	Size expected in the ith supernatant (S_i) in nm
S0	3 days sedimentation	$1000 \leq R_0$	$0 \leq S_0 \leq 1000$
S1	C: 30 min (S0) at 313 g	$450 \leq R_1 \leq 1000$	$0 \leq S_1 \leq 450$
S2	C: 1 h (S1) at 700 g	$200 \leq R_2 \leq 450$	$0 \leq S_2 \leq 200$
S3	C: 4 h (S2) at 1200 g	$70 \leq R_3 \leq 200$	$0 \leq S_3 \leq 70$
S3.5	UC: 30 min (S3) at 26 000 g	$50 \leq R_{3.5} \leq 70$	$0 \leq S_{3.5} \leq 50$
S3.5^{UC}	UC: 30 min (S0) at 26 000 g ^a	$50 \leq R_{3.5}^{UC}$	$0 \leq S_{3.5}^{UC} \leq 50$
S3.5^{UC, FA}	UC: 30 min (S0) at 26 000 g ^a	$50 \leq R_{3.5}^{UC, FA}$	$0 \leq S_{3.5}^{UC, FA} \leq 50$

184 ^a: one step ultra-centrifugation from a colloidal dispersion S0 obtained after stirring and sedimentation of a
 185 MX80 dispersion at 10 g/L in presence or absence of 11.8 mg/L FA .

186 The pH of all isolated supernatants is measured over a four months' time period and remains
 187 stable at 9.4 ± 0.2 . All the collected supernatants and solid residues are stored at +4°C in
 188 darkness before characterization and use in stability studies.

189 **2.3 Characterization of the clay colloidal dispersions**

190 **2.3.1 Ion and clay particle concentrations determination**

191 The element compositions are determined in all dispersions over time by Ion Chromatography
192 (IC, ICS-3000) and ICP-OES (Optima 2000 DV, PerkinElmer). The samples are acidified
193 before the ICP-OES measurements in 2% HNO₃ (Merck, ultrapure) plus a drop of HF (Merck,
194 suprapure, 48%).

195 **2.3.2 Mineral phase composition**

196 Mineral phases composing the clay particle dispersions and the solid residues are determined
197 by XRD. The aim is to detect possible differences in the composition between the different
198 size fractions. XRD data are collected on residuals and supernatants prepared as oriented
199 samples obtained by drying on sample holders (low background Si wafers). The residuals are
200 prepared by dilution of the solid-gel like dispersions in ultra-pure water. The SGW alone is
201 also analyzed as a reference to identify any phase that could precipitate in the supernatants or
202 residuals upon drying. X-ray diffractograms for all samples (raw MX-80, the supernatants and
203 the residues) are also collected after saturation with ethylene glycol (SIF-4). Powder
204 diffractograms are recorded with a D8 Advance (Bruker) diffractometer (Cu K_α radiation)
205 equipped with an energy dispersive detector (Sol-X). The phases are identified with the
206 DIFFRAC.EVA version 2.0 software (Bruker) by comparison with the JCPDS 2 database.

207 **2.3.3 Content of organic matter**

208 The total amount of organic carbon in the dispersions prepared in presence of FA is measured
209 with a TOC analyser (TOC-5000, Shimadzu). A change in the FA concentration is obtained
210 after ultra-centrifugation (final [FA] = 8.3 mg/L compared to 11.8 mg/L initially). This result
211 indicates that a third of the organic matter might be associated with the clay aggregates while
212 most of the FA (two thirds) remains in the dispersion under the present experimental
213 conditions, as expected for these small-sized molecules and at the present pH.

214 **2.3.4 Size distribution measurements**

215 The size distributions of montmorillonite aggregates in all dispersions are determined by
216 Photon Correlation Spectroscopy (PCS, homodyne single beam ZetaPlus System equipped
217 with a 50mW solid-state laser emitting at 632 nm, Brookhaven Inc, USA) and Asymmetric
218 Flow Field-Flow Fractionation system (AsFIFFF, HRFFF 10.000 AF4, Postnova Analytics,
219 Landsberg, Germany) coupled to a UV-Vis. detector (LambdaMax LC Modell 481, Waters,
220 Milford, USA) and an Inductively-Coupled Plasma-Mass Spectrometer (ICP-MS, X-Series2,
221 Thermo Scientific, Germany).

222 AsFIFFF/UV-Vis./MALLS/ICP-MS has previously been used for characterization of natural
223 or synthetic clays colloids (Bouby et al., 2012; Bouby et al., 2011; Bouby et al., 2004; Finck
224 et al., 2012; Plaschke et al., 2001). In this study, the clay dispersions obtained after
225 fractionation $(Si)_{i=0-3.5}$ are diluted to ~20 mg/L clay particles in SGW before injection into
226 the system. Details on the equipment, the fractionation conditions and the calibration are
227 given in the supporting information file (SIF-3).

228 For the PCS measurements, the clay dispersions are diluted to 10 mg/L in a disposable plastic
229 cuvette and measured over 5 runs consisting of 10 measurements of 15 s each, i.e. 50
230 measurements, for determination of mean hydrodynamic diameters.

231

232 **2.4 Clay particle stability studies**

233 Stability studies are performed using PCS-measurements according to the experimental
234 protocol described in (Behrens et al., 2000; Czigány et al., 2005; Holthoff et al., 1996;
235 Kretzschmar et al., 1998). The particle stability ratios (W) are calculated from the initial

236 agglomeration rates. The stability ratio is defined as the ratio between the fast agglomeration
237 rate to the measured agglomeration rate in the present sample:

$$238 \quad W = \frac{\left[\left(\frac{dr_h}{dt}\right)_{t \rightarrow 0} / C\right]^{(f)}}{\left[\left(\frac{dr_h}{dt}\right)_{t \rightarrow 0} / C\right]} \quad \text{Equation 1}$$

239 where r_h is the hydrodynamic radius (nm), t the time (s) and C the particle concentration
240 (mg/L), the suffix f represents the fast agglomeration rate. Equation 1 is derived from the
241 following Equations 2 and 3:

$$242 \quad \left(\frac{dr_h}{dt}\right)_{t \rightarrow 0} = \beta k C \quad \text{Equation 2}$$

$$243 \quad W = \frac{k^{(f)}}{k} = \frac{1}{\alpha} \quad \text{Equation 3}$$

244 where β is an optical factor (depending on the scattering angle, the wavelength of the light
245 and the particle radius), k is the agglomeration rate and α is the particle-particle attachment
246 efficiency and so-called the sticking probability. Consequently, W approaches 1 when the
247 particles are unstable under the chemical conditions tested, while for stable dispersions, W
248 tends to go to infinity (set arbitrarily to 10^1 - 10^2 values in our experiments to fit into the
249 graphs).

250 In this study, W is determined at pH 7, while the ionic strength was varied between 0.01 and 3
251 M by using the electrolytes NaCl, CaCl₂ or MgCl₂. In addition, experiments in presence or
252 absence of FA are performed, since FA is known to stabilize montmorillonite particles
253 (Furukawa and Watkins, 2012). The clay particle concentration is fixed to 10 mg/L by prior
254 dilution throughout all measurements, and all the supernatants listed in Table 1 are studied.
255 The initial intensity-weighted hydrodynamic mean diameter is measured first during 45 s
256 before addition of the electrolyte to the dispersion. Thereafter, the evolution of the particle
257 hydrodynamic diameter is monitored, after affecting the dispersion by simultaneous addition

258 of concentrated electrolyte aliquots (NaCl, CaCl₂ or MgCl₂) and NaOH to reach the desired
259 chemical conditions. All samples are measured up to between 20 and 40 min after addition of
260 the electrolyte, with measurements of 15 s each. To investigate the effects of addition of FA, a
261 final concentration of 10.2 mg FA/L is added to all clay dispersions. Thereafter, 0.1 M CaCl₂
262 is added to the dispersions and the results are compared to measurements in absence of FA.
263 As the pH cannot be monitored at the same time in the cuvette used for the PCS measurement,
264 it is measured in parallel in a second cuvette with a dispersion of identical composition.
265 The initial agglomeration rate is determined by fitting a second-order polynomial to the
266 experimental data, using the first 15-35 data points of each set of data. The initial
267 agglomeration rates are then compared and normalized to the fastest initial agglomeration rate
268 (determined for each electrolyte at 3M IS) for each colloidal fraction to obtain the
269 corresponding W value.

270

271 **3 Results and Discussion**

272 *3.1 Characterization of the clay colloidal dispersions*

273 **3.1.1 Ion and colloid concentrations**

274 The concentrations of all analyzed elements are presented in Table 2, where the mean values
275 obtained from several measurements are given. The clay colloid concentrations ([Coll.]) are
276 calculated from Al-concentrations according to the theoretical structural formula (Karnland et
277 al., 2006). The molar ratios of the different elements are calculated from the ICP-OES- and
278 IC-results and may be compared to the theoretical values based on the assumed stoichiometry.

279 **Table 2: Element and colloid concentrations in the clay colloidal dispersions measured by ICP-OES and**
280 **IC and colloidal fraction distributions calculated from the mean concentration of four main and minor**
281 **clay constituents (Si, Al, Mg, and Fe). The recovered amount of colloids in the dispersions is presented as**

282 percentage compared to the initial colloidal concentration in S0. *: This corresponds to the amount of
 283 stable colloids in the dispersions after letting settle the dispersions during 2 months without any shaking.
 284 The elemental mole ratios are corrected by the free aqueous concentrations determined after the strongest
 285 ultracentrifugation, which are $7.5 \cdot 10^{-5}$ M Si, $4.1 \cdot 10^{-6}$ M Mg, $7.2 \cdot 10^{-7}$ M Fe, $3.7 \cdot 10^{-6}$ M Al and $8.5 \cdot 10^{-6}$ M Ca.

Dispersion	[Coll.] mg/L	[Al] mg/L	[Mg] mg/L	[Si] mg/L	[Fe] mg/L	[Ca] mg/L	[Na] mg/L	[F] mg/L	[SO ₄] mg/L	[Cl] mg/L
S0	1127 ± 170	133 ± 20	20 ± 2	382 ± 110	32 ± 2	8.6 ± 0.5	87 ± 1	2.9 ± 0.5	37 ± 3	5 ± 1
S1	746 ± 68	88 ± 8	13.6 ± 0.4	252 ± 70	21.4 ± 0.6	5.7 ± 0.1	82 ± 2	2.9 ± 0.5	37 ± 3	3.9 ± 0.3
S2	551 ± 34	65 ± 4	9.9 ± 0.6	178 ± 46	15 ± 2	4.0 ± 0.2	76 ± 2	2.9 ± 0.5	37 ± 4	3.9 ± 0.4
S3	280 ± 26	33 ± 3	5.5 ± 0.2	99 ± 25	8 ± 1	2.5	77	3.0 ± 0.4	37 ± 4	3.8 ± 0.2
S3.5	96 ± 6	11.3 ± 0.6	1.9 ± 0.1	40 ± 18	2.7 ± 0.1	1.1	73	2.9	36	3.6
S3.5 ^{UC}	90 ± 6	10.6 ± 0.6	1.8 ± 0.1	40 ± 18	2.8 ± 0.3	1.0	74	2.7	36	4.7
S3.5 ^{UC,FA}	125 ± 3	14.7 ± 0.3	2.5 ± 0.1	51 ± 18	3.5 ± 0.1	1.6	75	3.0	36	4.8
SGW						1.6	28	2.5	3.2	2.9
Dispersion	Si/Al mole ratio	Al/Mg mole ratio	Al/Fe mole ratio	Al/Ca mole ratio	Mg/Fe mole ratio	Recovered colloids (%)				
S0	2.7	6.0	8.6	23.9	1.4	100 ± 0 (43 ± 1*)				
S1	2.7	5.9	8.5	24.4	1.5	67 ± 4 (47 ± 2*)				
S2	2.6	6.0	9.0	26.4	1.5	48 ± 5 (43 ± 2*)				
S3	2.8	5.5	8.6	22.7	1.6	25 ± 2 (22 ± 1*)				
S3.5	3.0	5.6	8.7	22.0	1.6	9.4 ± 0.1				
S3.5 ^{UC}	3.2	5.6	7.9	23.8	1.4	9.0 ± 0.2				
S3.5 ^{UC,FA}	3.1	5.5	8.7	17.3	1.6	12.1 ± 0.1				
Theoretical values	2.49	6.62	7.57		1.14					

286

287 As expected, the montmorillonite colloid concentration decreases with the number of
288 sequential centrifugation steps, for increasing centrifugation speed and time (Table 2). There
289 is no doubt that the particles consist of montmorillonite in all dispersions as the Si/Al, Al/Mg,
290 Al/Fe and Mg/Fe mole ratios are in fair agreement with those obtained from the theoretical
291 structural formula of montmorillonite (Table 2). Molar element ratios in the clay fraction are
292 corrected for the free aqueous concentration of dissolved elements in the dispersions. These
293 free aqueous concentrations are obtained from the supernatant of a sample centrifuged at 235
294 000 g where all clay mineral particles are assumed to be removed (SIF-2). The calcium
295 concentrations in the dispersions decrease with increasing numbers of centrifugation steps
296 similar to the decrease of colloid concentrations (Table 2) suggesting its association to the
297 clay aggregates, possibly due to ion exchange binding at the permanently charged basal plane.
298 Even though calcium does not appear in the theoretical formula, it is known that unpurified
299 MX80 bentonite contains calcium based accessory minerals, like calcite (Bradbury and
300 Baeyens, 2002; Karnland et al., 2006; Vuorinen and Snellman, 1998).

301 In addition, the results show a direct release of several elements from the unpurified bentonite
302 to the SGW, which is here the background electrolyte (Table 2). A drastic increase of sodium
303 and sulfate and, to a lower extend, fluoride and chloride is observed as already reported in the
304 literature (Bradbury and Baeyens, 2002; Vuorinen and Snellman, 1998). This can be
305 explained, altogether, by the presence of NaCl (1.35 mmol/kg), fluorite (CaF₂), gypsum
306 (CaSO₄) and celestite (SrSO₄) in the unpurified MX80 (Bradbury and Baeyens, 2002;
307 Vuorinen and Snellman, 1998). The dissolution of NaCl from the unpurified starting material
308 cannot explain the large increase of sodium concentration in the supernatants. In addition, no
309 increase in Ca concentration is observed (the concentration of Sr is not measured). Cation
310 exchange reactions, where divalent cations (Ca/Sr) are favored over monovalent ones (Na),
311 may explain why the Na release is enhanced and no variation in Ca concentration is observed

312 (Gaucher et al., 2009). Another process involving dissolution of pyrite, which is found in the
313 XRD analysis (Figure 1), can explain the release of sulfate. However, this should be
314 accompanied by a drop of pH. Thus, it is not considered as the most important process.

315 **3.1.2 Colloidal distribution in the montmorillonite fractions and long-term stability of** 316 **the dispersions**

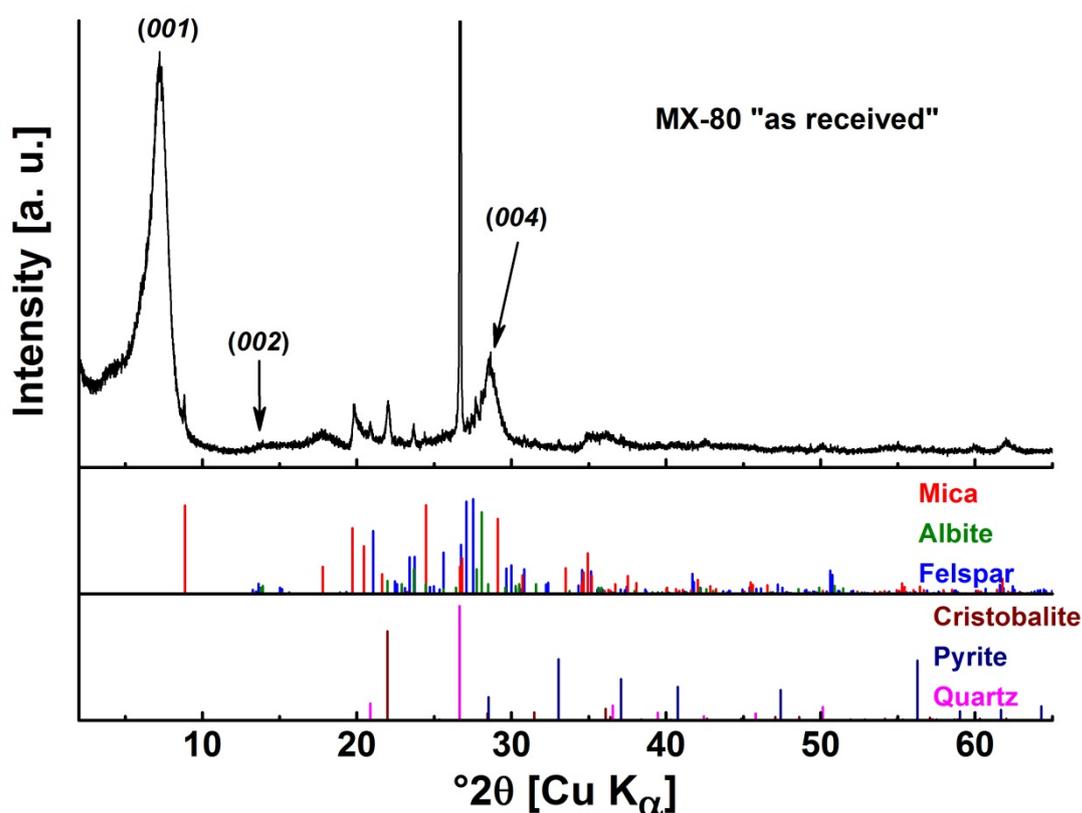
317 The mean clay colloidal concentrations after each centrifugation are calculated from the
318 concentrations obtained for the four main and minor montmorillonite constituents (Si, Al, Mg,
319 and Fe). They are compared to the initial concentration of colloids, which allows determining
320 the colloidal recoveries, Table 2.

321 From the total amount of colloids initially present in S0, approx. 9 % remain in the dispersion
322 S3.5 (Table 2) which is the dispersion obtained at the last fractionation step after using 27 000
323 g ultra-centrifugation. The similarity of the results obtained after one direct ultra-
324 centrifugation step (S3.5^{UC}, 9.0 ± 0.2 %) is noticeable. A slightly higher recovery of clay
325 colloids is obtained in presence of fulvic acids (S3.5^{UC,FA}, 12.1 ± 0.1 %), which indicates that
326 the negatively charged FA may have stabilized a part of the montmorillonite colloids initially
327 present in dispersion (Furukawa and Watkins, 2012; Kretzschmar et al., 1998).

328 To determine the long-term stability of the dispersions, the same analyses were performed 2
329 months later, without any shaking during that time or prior to the sampling. It is found that
330 not all dispersions are stable over time. This is particularly true for the dispersions S0 and S1
331 as indicated by the percentage of colloids recovered after 2 months (Table 2, marked with *)
332 showing that 57 % and 26 % of the clay colloids, respectively, have sedimented during this
333 time period. This indicates that these dispersions contain various sizes fractions, from large to
334 smaller clay aggregates, as expected from the sequential separation protocol.

335 **3.1.3 Mineral phase composition**

336 The as-received material, MX-80, consists mainly of montmorillonite, as indicated by the
 337 corresponding X-ray diffractogram (Figure 1). Accessory minerals are present in the
 338 unpurified bentonite such as quartz, cristobalite and mica, as well as trace amounts of albite,
 339 feldspar and pyrite. No attempt was made to quantify their content. This bentonite
 340 composition agrees well with reported data (Hu et al., 2009).

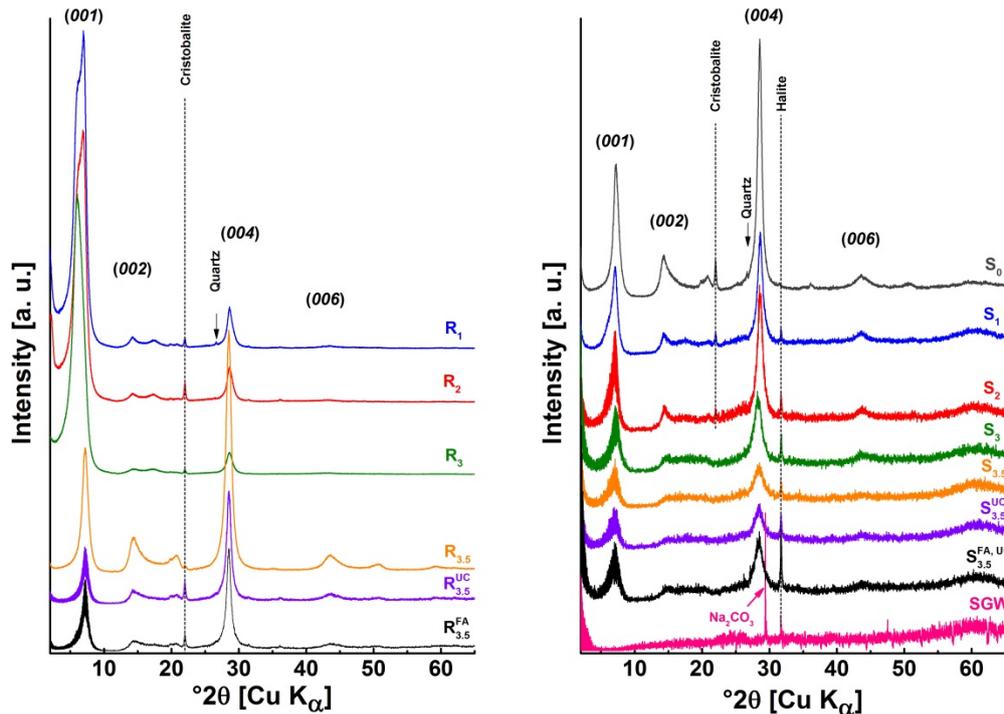


341
 342 **Figure 1: X-ray diffractogram of the as-received MX-80 and identification of the accessory minerals by**
 343 **comparison with database. Montmorillonite *00l* planes are indicated in brackets.**

344 The supernatants and residuals are all analyzed after each fractionation step (Figure 2). The
 345 solid material in R0 has identical mineralogical composition as the raw material. Obviously,
 346 the accessory phases settled down during the first fractionation step resulting in that
 347 cristobalite is detected only in the first sample and that quartz can be detected only in S0 and
 348 R1. All samples, both residuals and supernatants, exhibit intense reflections at 12.2–14.6 Å
 349 (7.2–6.0° 2θ) and ~ 3.14 Å (28.6° 2θ) corresponding to *001* and *004* reflections of

350 montmorillonite. The 001 reflection or basal spacing (i.e. $d(001)$), which corresponds to the c
351 dimension of the elemental unit cell, is dependent on the hydration state (Ferrage et al., 2005;
352 Meunier, 2005). In this study, all supernatants and residuals have a basal spacing
353 corresponding to the presence of one (12.2 Å) and two water molecules (14.6 Å) in the
354 interlayer. In R1 and R2, the clay is obviously heterogeneous in the hydration state as both
355 states may be present as shown by the broad 001 reflection. The clay interlayer hydration state
356 depends on the layer charge and the ambient relative humidity, not on the fractionation
357 procedure. All samples also exhibit less intense 001 reflections typical of clay minerals, such
358 as 002 and 006 . Finally, all residues have a similar mineralogical composition except the
359 quartz detected in trace amounts in R1. Likewise, all suspended particles in supernatants have
360 a similar mineralogical composition, except S0, S1 and S2 that contain cristobalite and S0 that
361 contains additionally trace amount of quartz. Finally, only halite (NaCl) and Na_2CO_3 could be
362 detected in SGW meaning that these phases crystallized upon drying. Halite could be detected
363 in some supernatants. None of these phases (NaCl or Na_2CO_3) could be detected in the
364 residues.

365 All supernatants and residuals exhibit similar basal spacing after saturation with ethylene
366 glycol (SIF-4). The expansion to 17.0 ± 0.2 Å for $d(001)$ is typical of smectite swelling, and
367 thus consistent with montmorillonite being the main component of MX-80.



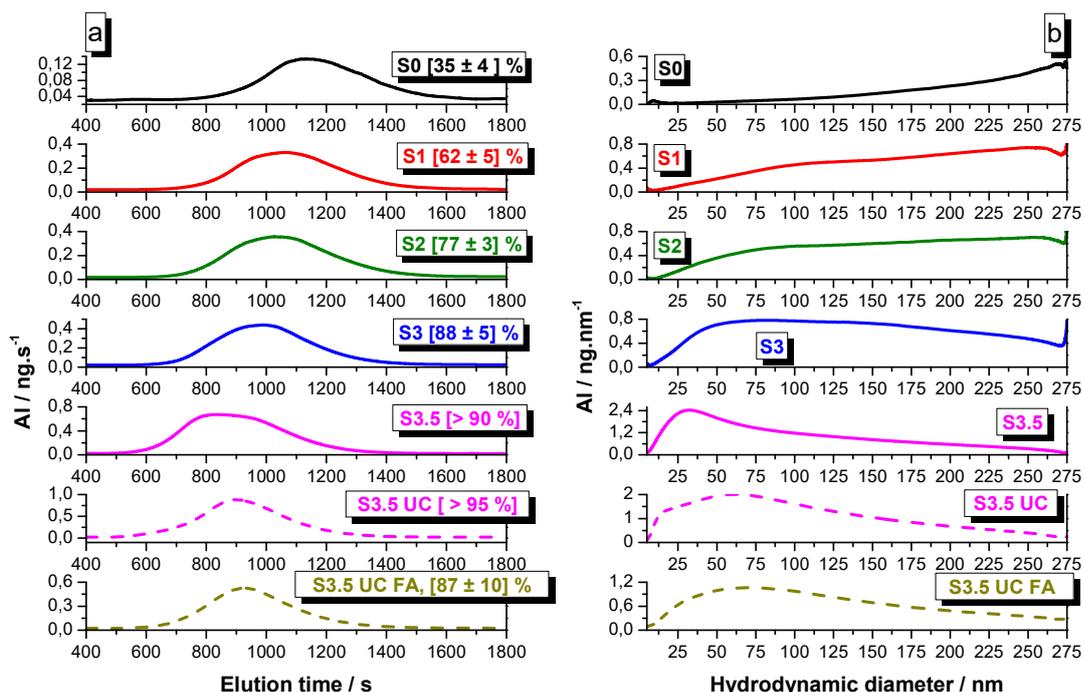
368

369 **Figure 2: X-ray diffractograms for all residuals (left) and supernatants (right) obtained by fractionation.**
 370 **One can see the similarities between the residuals and supernatants, which implies a similar structure of**
 371 **the montmorillonite in the different samples. In addition, a decrease in accessory minerals with the**
 372 **number of centrifugation steps is seen. The montmorillonite 00/ planes are indicated in brackets.**

373 **3.1.4 Clay aggregate size distribution measurements**

374 3.1.4.1 AsFIFFF

375 Since aluminium is one of the main components of montmorillonite, the Al-data obtained
 376 from the AsFIFFF/ICP-MS-measurements are used as a clay indicator. All Al-ICP-MS data
 377 are presented in Figure 3 after transformation of fractograms in mass versus size by using 1)
 378 the mass calibration method (left side, Figure 3a) as developed before in previous studies
 379 (Bouby et al., 2008) and 2) the size calibration (right side, figure 3b), according to (Schimpf
 380 et al., 2000).



381

382 **Figure 3: AI-ICP-MS fractograms obtained after injection (100 μ L) of the different clay dispersions, all**
 383 **diluted to 20 mg/L clay prior to injection. Left: fractograms transformed using the calibration in mass**
 384 **concentration as a function of elution time (Bouby et al., 2008). Right: fractograms further transformed**
 385 **by using the calibrations to size (Schimpf et al., 2000). The percentage in bracket indicates the colloid**
 386 **recovery in the measurements. These are all smoothed data and a mean result of two measurements.**

387 At a first look, a broad size distribution is obtained for each dispersion, ranging from 10 up to
 388 275 nm. Some shoulders are clearly visible in the fractograms, indicating the presence of
 389 different size fractions in the dispersions. A separation into different well-resolved size
 390 fractions is not achieved due to the conditions selected for the AsFIFFF measurements (see
 391 SIF-3). Nevertheless, the fractograms show clearly that the mean size of the aggregates in the
 392 dispersions is decreasing with the number of fractionation steps. This is clearly evidenced by
 393 the significant variation of the fractogram maxima and the mean sizes of the different
 394 colloidal dispersions (Figure 3 and Table 3).

395 **Table 3: Peak maxima and mean aggregate sizes of the dispersions obtained from AsFIFFF-ICP-MS**
396 **measurements with the corresponding mean intensity (I)- and volume (V)-weighted sizes determined from**
397 **PCS analysis from the multimodal size distribution (MSD). The colloid recovery in the AsFIFFF-**
398 **measurements increases with decreasing sizes. d_T/d_S : equivalent spherical diameter (ESD) ratios, where d_T**
399 **is the ESD for a translating disc-shaped particle determined by PCS (mean volume-weighted value, PCS_V)**
400 **and d_S is the equivalent Stokes' spherical diameter for a sedimenting particle determined by AsFIFFF**
401 **(mean value); ρ : calculated axial ratio, see section 3.1.4.2 for details.**

Sample	Mode (peak max.) (nm)			PCS	Mean (nm)			From (Jennings and Parslow, 1988)	
	AsFIFFF	Half- width	Recovery (%)	Average count rate (kcps)	PCS_I (MSD)	PCS_V (d_T) (MSD)	AsFIFFF (d_S)	d_T/d_S	ρ
S0	264 ± 9	64 ± 47	35 ± 4	118 ± 7	1452 ± 632	962 ± 225	229 ± 5	4.20	66.3
S1	243 ± 28	183 ± 24	62 ± 5	87 ± 2	513 ± 60	610 ± 57	198 ± 13	3.07	34.6
S2	255 ± 21	217 ± 4	77 ± 3	53 ± 1	404 ± 95	337 ± 29	189 ± 7	1.78	10.3
S3	80 ± 5	232 ± 18	88 ± 5	37 ± 1	248 ± 28	186 ± 64	151 ± 14	1.23	3.7
S3.5	33 ± 3	83 ± 15	> 90	20 ± 1	181 ± 28	172 ± 49	84 ± 8	2.06	14.4
S3.5 ^{UC}	61 ± 6	142 ± 12	> 95	25 ± 1	180 ± 39	167 ± 50	95 ± 13	1.76	10.0
S3.5 ^{UC, FA}	70 ± 6	167 ± 1	87 ± 10	29 ± 1	185 ± 47	143 ± 43	124 ± 24	1.16	3.0

402

403 The half-width values decrease only slightly for the dispersions S0 to S3.5 indicating that a
404 rather broad character of the size distributions remains. In addition, it should be noted that the
405 mean clay aggregate sizes obtained in the dispersions is higher than expected (Table 1),
406 especially for the dispersions where the smallest size is expected, i.e. in S3 and all S3.5
407 dispersions. This may be interpreted as an incomplete sedimentation during the centrifugation

408 due to the inaccurate assumption made considering a spherical shape of the particles in the
409 Stokes' law calculation, since the particle shape is of high importance while included in
410 Stokes' law (Kunkel, 1948).

411 The colloid recovery for each AsFIFFF-measurement (indicated in brackets in the legend in
412 Figure 3a and in Table 3, 4th column) can also help to understand the results. One explanation
413 for the low recoveries in S0 to S2 runs is the loss of particles in the AsFIFFF-channel due to
414 an irreversible attachment of notably larger sized aggregates to the membrane during the
415 fractionation process. The lower recovery of the Al-mass especially for the dispersions S0 and
416 S1 indicates the presence of large aggregates attaching to the accumulation wall in the
417 channel or moving too slowly to be detected under these conditions. This is in agreement with
418 the slow sedimentation process observed in the unstirred dispersions S0 and S1 over time
419 (Table 2). The recovery increases significantly with higher centrifugation forces, where higher
420 recoveries are reached for the dispersions obtained after the ultra-centrifugation step (S3.5 and
421 S3.5^{UC}).

422

423 3.1.4.2 PCS

424 To complement the AsFIFFF analysis, the dispersions are monitored by PCS after dilution to
425 10 mg/L clay. The results of the PCS analyses are presented in Table 3. The table presents the
426 average count rates (in kilo counts per second (kcps)) which clearly decrease for
427 centrifugation steps with higher rotation rates, even though the colloid mass concentrations
428 are the same. Since the scattered intensity is highly dependent on the particle size, this is in
429 line with the size variations seen in the AsFIFFF-measurements (Table 3). The corresponding
430 values for the mean diameters of the clay aggregates are given, both as intensity-weighted
431 (PCS_I) and as volume-weighted (PCS_V) in Table 3 as obtained from the measurements by

432 considering the multimodal size distribution using the Non-Negatively constrained Least
433 Squares (NNLS) algorithm to fit the data (Bro and De Jong, 1997). The volume-weighted
434 diameter values (PCS_V) are those which can be compared directly with the AsFIFFF data.
435 Looking into Table 3 (column 7 and 8), the results are comparable. The differences are
436 explained by losses of large particles in the AsFIFFF channel (especially for samples S0 and
437 S1) and by recalling that the PCS preferentially detect larger sized entities.

438 Nowadays, it is recognized that several techniques have to be used to combine the results
439 from particle size measurements and draw a more realistic description of a natural or synthetic
440 sample, containing particles of irregular shapes, especially clay nanoparticles (Beckett et al.,
441 1997; Bowen, 2002; Bowen et al., 2002; Cadene et al., 2005; Gallego-Urrea et al., 2014;
442 Gantenbein et al., 2011; Plaschke et al., 2001; Veghte and Freedman, 2014). More
443 information can be obtained from the AsFIFFF and PCS data following the development of
444 (Jennings and Parslow, 1988) extended by e.g. (Bowen et al., 2002), (Pabst and Berthold,
445 2007) and (Gantenbein et al., 2011). In brief, whatever equipment is used, the dimensions
446 obtained are equivalent sphere diameters (ESD) i.e. the diameters of spheres that would
447 behave the same as the particles in the sample, as a function of the method used. One should
448 have in mind that the ESD describes a 3-dimensional object with only one number. Flow FFF
449 provides a direct access to the Stokes' diameter d_s (Schimpf et al., 2000). "Particles under the
450 influence of Brownian agitation translate for all orientations and it is the random orientation
451 translation that is analysed in the PCS method" (Jennings and Parslow, 1988). Accordingly,
452 the PCS gives access to the equivalent diameter from frictional translatory diffusion data, d_T .
453 Consequently, except for spherical particles, one cannot expect the derived ESD to be
454 identical from the two techniques as different physical phenomena are the basis of the
455 measurements. This is used presently as an advantage considering that no identical results
456 reveal the non-sphericity of the particles to be analysed and can thus serve to measure it. We

457 develop that possibility in the following discussion by comparing the ESD values (d_S)
 458 obtained with the AsFIFFF and the ESD values (d_T) obtained with the PCS, i.e. the volume-
 459 weighted ones from the MSD fitting.

460 According to Jennings (Jennings, 1993), a comparison between the ESD values from the
 461 AsFIFFF (d_S) and PCS (d_T) gives access to the mean clay axial ratio (ρ) for the aggregates in
 462 each dispersions defined as the aggregate surface diameter to thickness ratio for each
 463 dispersions. In previous works (Jennings, 1993; Jennings and Parslow, 1988), Jennings
 464 presents the mathematical expressions of the equivalent spherical diameter (ESD) according
 465 to the analytical method used for its determination which are functions of the axial ratio. The
 466 equations are given primarily for oblate and prolate spheroids with two limiting geometry
 467 cases considered: the rod and the disc (to which the clay aggregate geometry may be
 468 simplified). The ESD for a translating disc-shaped particle (d_T) and the equivalent Stokes'
 469 diameter (d_S) for a sedimenting particle are expressed in equation (4) and (5) as (Jennings and
 470 Parslow, 1988):

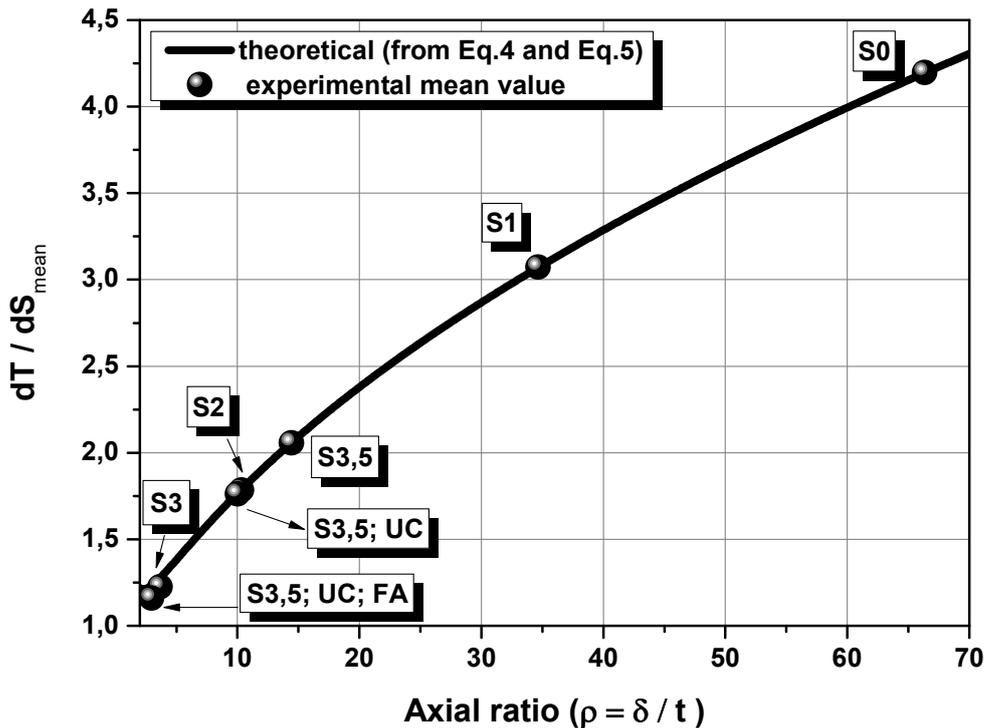
$$471 \quad \frac{d_T}{\delta} = \frac{\sqrt{\rho^2 - 1}}{\rho \cdot \arctan(\sqrt{\rho^2 - 1})} \quad \text{Equation 4}$$

$$472 \quad \frac{d_S}{\delta} = \sqrt{\frac{\arctan(\sqrt{\rho^2 - 1})}{\sqrt{\rho^2 - 1}}} \quad \text{Equation 5}$$

473 where $\rho = \delta/t$ is the axial ratio of the disc-shaped particle, with δ being the surface diameter
 474 of the disc-shaped particle and t its thickness.

475 Consequently, for a given particle, the ratio of these two ESD expressions may be used
 476 inversely *a posteriori* to evaluate the axial or aspect ratio (ρ) of the particle and thus to obtain
 477 the value of δ and t , if the clay aggregate is approximated by a disc of diameter δ and
 478 thickness t . In the present work, the ratio d_T/d_S correspond to the ratio of the ESD determined

479 by AsFIFFF (d_S) and PCS (d_T) (volume-weighted mean value, PCS_v). The calculated d_T/d_S
 480 from the experimental mean diameters are presented in Table 3. The theoretical curve
 481 $d_T/d_S = f(\rho)$ obtained from Equation 4 and Equation 5 is plotted in Figure 4 and is used to
 482 deduce the axial ratio (ρ) for each clay colloid dispersion reported in Table 3.



483

484 Figure 4: Theoretical d_T/d_S -ratio values calculated as a function of the axial ratio (black line) using
 485 equations (4) and (5). The d_T/d_S -ratio values determined from the experimental mean PCS and AsFIFFF
 486 ESD data are reported for each dispersion. *A posteriori*, the corresponding axial ratio is obtained and
 487 presented in Table 3.

488 Obviously, $\rho > 1$ for each dispersion as expected for clay aggregates having a disc-shaped
 489 geometry. Interestingly, the ρ -values are decreasing with increasing fractionation steps from
 490 ~ 35 (S1) down to ~ 3.7 (S3). (Note: due to the low AsFIFFF recovery, the ρ -value obtained for
 491 S0 (~ 66) is biased).

492 Once ρ -values are known for each dispersion, one can back-calculate the corresponding mean
493 surface diameter, δ , and thickness, t , by using Equation 4 and Equation 5. The number of clay
494 layers is calculated by taking 1.3 nm as the thickness of one single clay mineral layer (basal
495 spacing) obtained by XRD results and according to (Meunier, 2005). The results are
496 summarized in Table 4. According to literature, the clay aggregates dimensions reported in
497 this work are plausible (Bergaya et al., 2006; Bouby et al., 2011; Hauser et al., 2002; Missana
498 et al., 2003; Plaschke et al., 2001; Schramm and Kwak, 1982a, b; Sposito, 1992; Tournassat et
499 al., 2011; Tournassat et al., 2003). The aspect ratio values determined agree with literature
500 data (Ali and Bandyopadhyay, 2013; Cadene et al., 2005; Gélinas and Vidal, 2010; Plaschke
501 et al., 2001; Tournassat et al., 2011; Tournassat et al., 2003; Weber et al., 2014; Veghte and
502 Freedman, 2014). Pictures obtained from SEM analysis of the dispersions S0 to S3 are
503 presented in the supporting file (see SIF-5). A raw evaluation of the AsFIFFF/MALLS data
504 according to (Baalousha et al., 2005; Baalousha et al., 2006; Kammer et al., 2005) allows to
505 compare the hydrodynamic (R_h) versus gyration (R_g) radius. The corresponding ratio (R_g/R_h),
506 called the shape factor, varies in the range [1.5-4] for the present measurements, and equals to
507 1 for a spherical particle. The shape factor increases as soon as the particles deviate from a
508 spherical shape, indicating that the montmorillonite aggregates are non-spherical.

509 **Table 4: Mean disc surface diameters (δ) and number of layers calculated from PCS and AsFIFFF mean**
510 **equivalent sphere diameters (ESD) and the mathematical equations 4 and 5, according to (Jennings and**
511 **Parslow, 1988) for the clay aggregates. The number of layers is calculated by taking 1.3 nm as the**
512 **thickness, t , of one clay sheet, according to XRD results when considering one water layer.**

Sample	Axial ratio $\rho = \delta t$	PCS d_t/δ	AsFIFFF d_s/δ	δ (disc \emptyset ; nm)	t (disc thickness; nm)	Number of layers
S0	66.3	0.643	0.226	1496	23	17
S1	34.6	0.648	0.325	940	27	21
S2	10.3	0.675	0.449	500	48	37

S3	3.7	0.743	0.546	250	68	52
S3.5	14.4	0.664	0.303	258	18	14
S3.5 ^{UC}	10.0	0.676	0.385	246	25	19
S3.5 ^{UC,FA}	3.0	0.767	0.546	187	63	48

513

514 By plotting the oblate spheroid ESD as a function of the axial ratio (Jennings and Parslow,
515 1988), the ESD is found to always be smaller than the true dimension, δ . This is true for both
516 measurement techniques used in this study as well (Table 4). From S0 to S3, there is a clear
517 trend in decreasing surface diameter, δ , and increasing thickness, t . Nevertheless, the AsFIFFF
518 results are obtained from measurements with rather low recoveries while the PCS is detecting
519 all aggregates in the dispersion. Consequently, the results presented in Table 4 can only be
520 considered as partly representative of the complete samples due to the low recoveries in the
521 AsFIFFF-measurements. If one considers the dispersions where $\geq 50\%$ of the mass is
522 recovered (S1 and smaller), the mean disc surface diameter (δ) of the clay aggregates is
523 decreasing, whereas the thickness (t) is increasing with further fractionation steps. The
524 difference between the dispersion S3 and S3.5 appears only in the thickness of the clay
525 aggregates. As expected, comparable results are obtained for the dispersions S3.5 (obtained
526 after continuous (ultra-)centrifugation steps) and S3.5^{UC} (obtained after one single ultra-
527 centrifugation step). Interestingly, the thickness, and thus number of clay sheets, appears
528 slightly higher in presence of FA during the fractionation, which may indicate that the
529 presence of FA could stabilize thicker clay aggregates, i.e. maintain a larger number of
530 stacked clay mineral layers together.

531 In conclusion, the fractionation protocol developed in the present study enables to obtain
532 heterogeneous dispersions of clay aggregates. Assimilating the clay aggregates to discs of
533 surface diameter δ and thickness t , the results indicate presence of aggregates with mean

534 surface diameters ranging from ~245 nm up to 1500 nm and with mean thicknesses ranging
 535 from ~18 up to 70 nm (~14 to 52 clay layers). In presence of FA during the fractionation, clay
 536 aggregates with a surface diameter of ~190 nm can be isolated, but with a slightly larger
 537 thickness (~63 nm) as those obtained under the same fractionation conditions in absence of
 538 FA. The present results would greatly benefit of complementary investigations involving the
 539 use of other microscopy techniques like AFM.

540 3.1.5 An attempt to estimate the mean number of edge sites

541 By approximating clay aggregates to discs of mean diameter δ , estimations of the mean
 542 number of edge sites in each clay dispersion were performed. This will be used in an attempt
 543 for better interpretation of the data for radionuclides sorption by surface complexation and
 544 sorption reversibility (manuscripts in preparation).

545 Estimations of the number of edge sites are performed according to the work of White and
 546 Zelazny (White and Zelazny, 1988) and Tournassat et al. (Tournassat et al., 2003), assuming a
 547 clay density of 2.7 g/cm³, and are presented in Table 5. It is considered that the stacking of
 548 clay mineral layers does not change the accessibility to the lateral surfaces, only the interlayer
 549 basal surfaces are not accessible.

550 **Table 5: Estimation of the mean number of edge sites for each clay dispersion from PCS- and AsFIFFF-**
 551 **data. The perimeter of a clay stack is noted as P and is calculated by using the clay aggregate disc**
 552 **diameter δ . The clay disc area (A) is calculated by using δ as the mean diameter of the clay aggregate as**
 553 **well. .**

Samples	δ (nm)	Ratio (P/A) nm ⁻¹	n _{Al} mmol/kg	n _{Si} mmol/kg	n _{Tot} mmol/ kg
S0	1496	0.0027	4.9	6.3	11.2
S1	940	0.0042	7.8	10.0	17.8
S2	500	0.0080	14.7	18.8	33.5

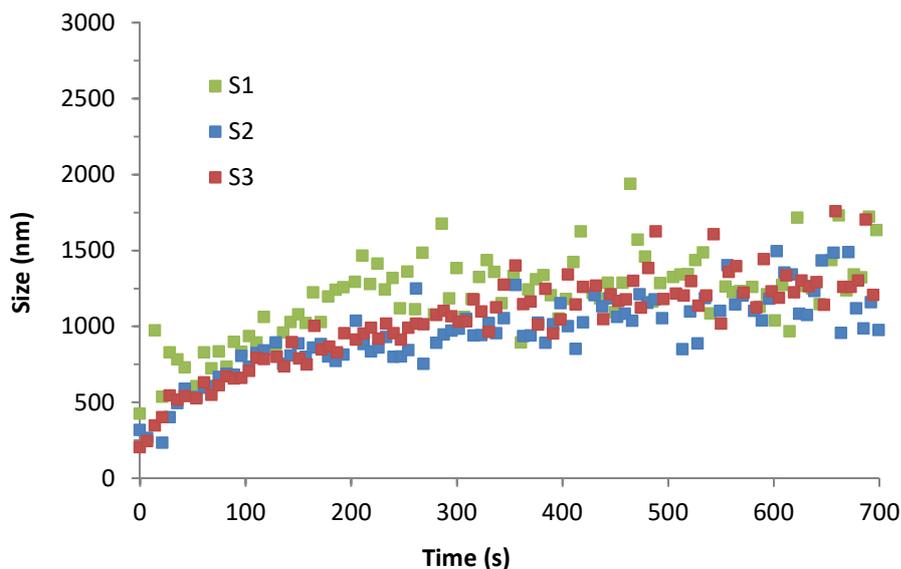
S3	250	0.0161	29.4	37.6	67.0
S3.5	258	0.0152	28.4	36.3	64.7
S3.5 ^{UC}	246	0.0162	29.8	38.1	67.9
S3.5 ^{UC,FA}	187	0.0214	39.3	50.2	89.5

554

555 The results show variations up to a factor ~ 8 , but they are only considered as approximations
556 since the aggregate dimensions are underestimated. Taking a regular disc to mimic smectite
557 aggregates does not take into account their convexities and concavities which lead to an
558 increase in their surface area and perimeter. When considering the dispersions with the
559 smaller mean clay size (S3.5, S3.5^{UC} and S3.5^{UC,FA}), the results are in agreement with those of
560 Tournassat et al. (Tournassat et al., 2003).

561 *3.2 Stability studies*

562 Evaluation of the Al-AsFIFFF/ICP-MS fractograms for the montmorillonite fractions reveals
563 broad clay aggregate size distributions that might be constituted by several different clay size
564 fractions (Figure 3). Consequently, it is not surprising that the data obtained from the stability
565 studies are very scattered (Figure 5). Therefore, it becomes challenging to clearly observe the
566 increase in mean particle size which reflects the agglomeration rate (especially for the
567 dispersion S0 which will not be further considered). In addition, one has to consider that the
568 agglomeration behavior of smaller sized particles are probably hidden by the dominant
569 scattered light intensities from larger particles as the PCS preferentially detect those larger
570 sized entities. Nevertheless, the results from the data evaluation are less scattered for the
571 dispersions obtained after several centrifugation steps (S3 and S3.5).



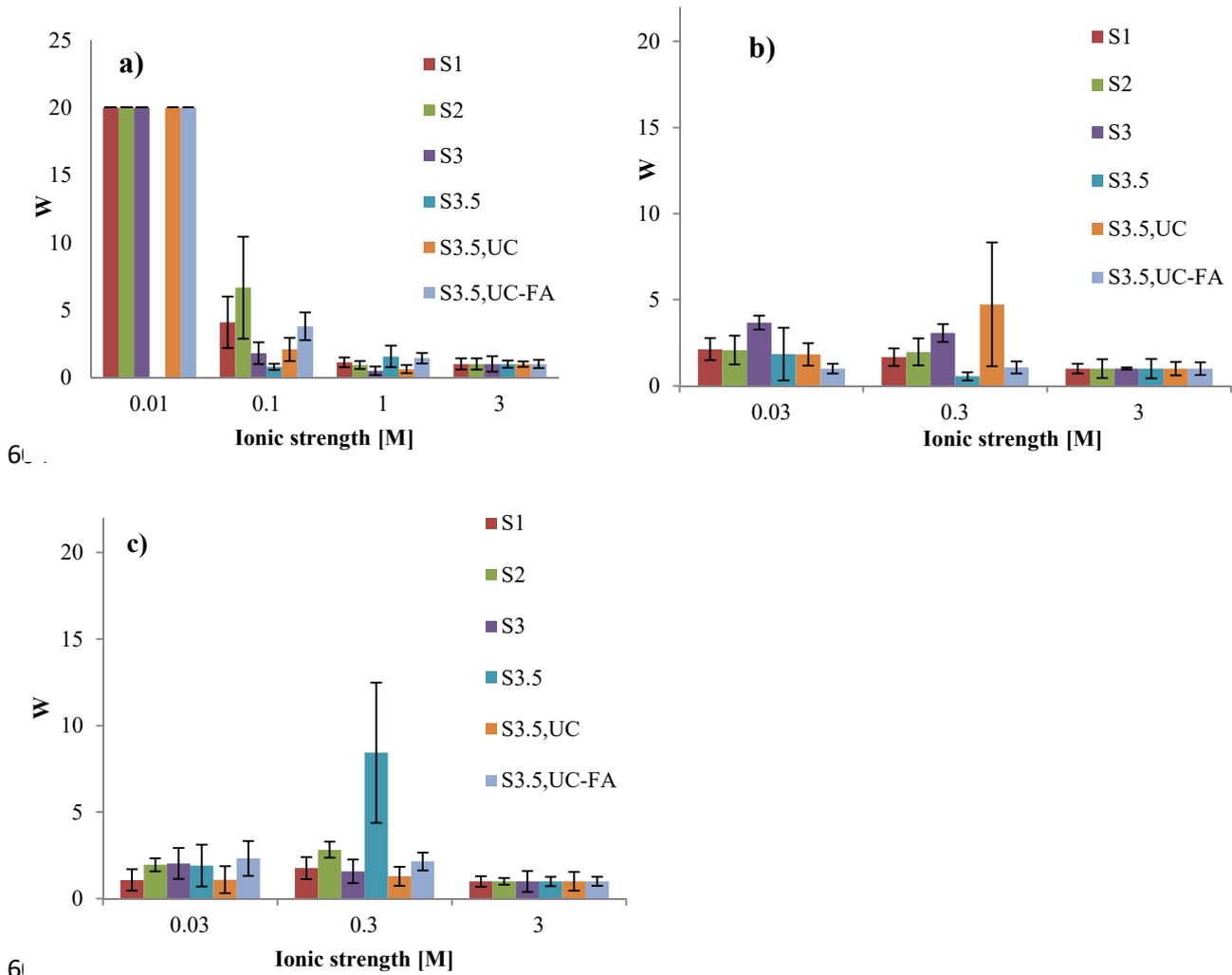
572

573 **Figure 5: Increase in hydrodynamic diameter for three of the montmorillonite dispersions while adding**
 574 **0.01 M CaCl₂ to the dispersions at pH 7.**

575

576 The calculated stability ratios (W) for all dispersions at pH 7 and for different ionic strengths
 577 are presented in Figure 6. The presented W-values are obtained for an ionic strength set by
 578 addition of the electrolytes NaCl, CaCl₂ or MgCl₂. As expected, W decreases with increasing
 579 ionic strength. This is clearly seen after addition of NaCl (Figure 6a) and is consistent with
 580 the DLVO-theory. Furthermore, addition of CaCl₂ and MgCl₂ affects the montmorillonite
 581 particles more strongly than addition of the same ionic strength set by NaCl since the lowest
 582 concentrations of CaCl₂ and MgCl₂ are already enough to destabilize the montmorillonite
 583 particles (Figure 6b and 6c), as expected from previous studies (Schudel et al., 1997). This is
 584 in line with the well-known Schulze-Hardy rule (Overbeek, 1980). The decrease in stability
 585 ratio in presence of divalent cations is partly explained by specific interaction of divalent
 586 cations as previously reported in the literature (French et al., 2009; Keiding and Nielsen,
 587 1997; Norrfors, 2015; Oncsik et al., 2014; Pantina and Furst, 2006).

588 According to the DVLO-theory, considering the interaction between two identical spherical
589 particles, the calculated Van der Waals (VdW)-forces increase for increasing particle size
590 (Ottewill and Shaw, 1966; Reerink and Overbeek, 1954; Shah et al., 2002). However, it has
591 been found previously that in a system of high ionic strength, i.e. where no electrostatic
592 repulsions are present, the kinetic energy dominates over the VdW-forces and the
593 agglomeration rate constants of spherical latex particles are therefore independent of the
594 particle size (Norrfors, 2015). Even though clay aggregates are known to have different
595 shapes and compositions than the latex particles present in the previous study (Norrfors,
596 2015), the domination of the kinetic energy can be one explanation of the absence of
597 significant differences between the colloidal dispersions in this study (Figure 6). The absence
598 of particle size dependency on the stability ratios is further in agreement with previous studies
599 (Behrens et al., 2000; Ottewill and Shaw, 1966) but once again, one should have in mind that
600 PCS measurements in polydisperse dispersions favour larger sized particles and thereby
601 hiding the agglomeration behaviour of the smaller sized ones. Previous studies of
602 polydisperse dispersions (Chang and Wang, 2004; Jia and Iwata, 2010) indicate that their
603 stability ratio is smaller than for a mono disperse system, which may be seen in this study.



606
607 **Figure 6: Stability ratios for the colloidal dispersions after addition of a) NaCl b) CaCl₂ or c) MgCl₂, at pH**
608 **7. Infinity is set to 20 in the figures.**

609
610 Finally, no significant differences in stability are observed in presence or absence of FA in the
611 dispersions. Previous studies present a stabilization of the clay particles in presence of FA
612 (Kretzschmar et al., 1998) and notice that the stabilization properties of FA decreases with
613 increasing pH, due to the lower FA adsorption to clay surfaces. In the present study of
614 agglomeration, caused by addition of CaCl₂, the relative high concentration of divalent ions,

615 Ca^{2+} , induced agglomeration with the same agglomeration rate in both presence and absence
616 of FA.

617 **4 Conclusions**

- 618 • A protocol to obtain montmorillonite colloid dispersions with different size fractions
619 is developed in this study. It is based on a sedimentation step followed by sequential
620 or direct (ultra-)centrifugation.
- 621 • Montmorillonite aggregates of same composition are proved to be present in the
622 different dispersions as concluded from both the chemical analysis and the XRD
623 results. Calcium is associated to the clay particles as natural calcite or due to the fast
624 ionic exchange processes arising under the present experimental conditions. An instant
625 release of sodium and sulfate occurs when the bentonite is suspended in the SGW.
626 This is explained by dissolution of gypsum or/and celestite naturally present in the
627 unpurified MX-80 bentonite.
- 628 • Mean equivalent sphere diameters (EDS) values obtained by different methods agree
629 when normalized to comparable physical properties, leading to a mean hydrodynamic
630 size of the clay aggregates from ~ 960 nm down to ~ 85 nm. Nevertheless, after
631 applying mathematical treatments, the differences recorded in the initial data between
632 the AsFIFFF (giving the Stokes' diameter) and the PCS (giving a frictional translatory
633 diffusion diameter) are used to estimate the mean diameter δ and the thickness t of the
634 clay aggregates in the different dispersions after approximating those to regular disc-
635 shaped aggregates consisting of stacked clay mineral layers. According to our
636 calculation, δ varies from $1.5 \mu\text{m}$ down to ~ 190 nm and t lies in the range of 18 to 70
637 nm. The number of sheets (clay mineral layers) is determined by dividing the
638 thickness t by 1.3 nm (thickness of one single clay layer in basal spacing). The

639 corresponding axial (or aspect) ratios ($\rho = \delta/t$) calculated in this study agree well with
640 literature data. Further calculations, based on literature, give an estimation of the
641 number of edge sites in each clay dispersion. These data will be used in an attempt to
642 model the results from radionuclides sorption experiments performed by using these
643 clay dispersions (manuscript in preparation).

- 644 • The stability of montmorillonite is higher in NaCl solution than in CaCl₂ and MgCl₂
645 for the same ionic strength, which is in line with the Schulze-Hardy rule. In addition,
646 the stability ratio is independent on the colloidal size initially present.

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651 10.

652 *References*

653 Ali, S., Bandyopadhyay, R., 2013. Use of Ultrasound Attenuation Spectroscopy to Determine
654 the Size Distribution of Clay Tactoids in Aqueous Suspensions. *Langmuir* 29, 12663-12669.

655 Baalousha, M., Kammer, F.D., Motelica-Heino, M., Le Coustumer, P., 2005. 3D
656 characterization of natural colloids by FIFFF-MALLS-TEM. *Anal Bioanal Chem* 383, 549-
657 556.

658 Baalousha, M., Kammer, F.V.D., Motelica-Heino, M., Hilal, H.S., Le Coustumer, P., 2006.
659 Size fractionation and characterization of natural colloids by flow-field flow fractionation
660 coupled to multi-angle laser light scattering. *Journal of Chromatography A* 1104, 272-281.

661 Beckett, R., Murphy, D., Tadjiki, S., Chittleborough, D.J., Calvin Giddings, J., 1997.
662 Determination of thickness, aspect ratio and size distributions for platey particles using
663 sedimentation field-flow fractionation and electron microscopy. *Colloids and Surfaces A:
664 Physicochemical and Engineering Aspects* 120, 17-26.

665 Behrens, S.H., Christl, D.I., Emmerzael, R., Schurtenberger, P., Borkovec, M., 2000.
666 Charging and Aggregation Properties of Carboxyl Latex Particles: Experiments versus
667 DLVO Theory. *Langmuir* 16, 2566-2575.

668 Bergaya, F., Theng, B.K.G., Lagaly, G., 2006. *Handbook of Clay Science*.

669 Bessho, K., Degueldre, C., 2009. Generation and sedimentation of colloidal bentonite
670 particles in water. *Applied Clay Science* 43, 253-259.

671 Bhatia, M.P., Das, S.B., Longnecker, K., Charette, M.A., Kujawinski, E.B., 2010. Molecular
672 characterization of dissolved organic matter associated with the Greenland ice sheet.
673 *Geochim. Cosmochim. Acta* 74, 3768-3784.

674 Bouby, M., Finck, N., Geckeis, H., 2012. Flow field-flow fractionation (FIFFF) coupled to
675 sensitive detection techniques: a way to examine radionuclide interactions with nanoparticles.
676 *Mineralogical Magazine* 76, 2709-2721.

677 Bouby, M., Geckeis, H., Geyer, F.W., 2008. Application of asymmetric flow field-flow
678 fractionation (AsFIFFF) coupled to inductively coupled plasma mass spectrometry (ICPMS)
679 to the quantitative characterization of natural colloids and synthetic nanoparticles. *Anal
680 Bioanal Chem* 392, 1447-1457.

681 Bouby, M., Geckeis, H., Lutzenkirchen, J., Mihai, S., Schafer, T., 2011. Interaction of
682 bentonite colloids with Cs, Eu, Th and U in presence of humic acid: A flow field-flow
683 fractionation study. *Geochim. Cosmochim. Acta* 75, 3866-3880.

684 Bouby, M., Geckeis, H., Manh, T.N., Yun, J.-I., Dardenne, K., Schäfer, T., Walther, C., Kim,
685 J.-I., 2004. Laser-induced breakdown detection combined with asymmetrical flow field-flow
686 fractionation: application to iron oxi/hydroxide colloid characterization. *Journal of*
687 *Chromatography A* 1040, 97-104.

688 Bowen, P., 2002. Particle Size Distribution Measurement from Millimeters to Nanometers
689 and from Rods to Platelets. *Journal of Dispersion Science and Technology* 23, 631-662.

690 Bowen, P., Sheng, J., Jongen, N., 2002. Particle size distribution measurement of
691 anisotropic—particles cylinders and platelets—practical examples. *Powder Technology* 128,
692 256-261.

693 Bradbury, M.H., Baeyens, B., 2002. Porewater chemistry in compacted re-saturated MX-80
694 bentonite: Physico-chemical characterisation and geochemical modelling PSI Bericht Nr. 02-
695 10, 28.

696 Bro, R., De Jong, S., 1997. A fast non-negativity-constrained least squares algorithm. *Journal*
697 *of chemometrics* 11, 393-401.

698 Brown, G.H., 2002. Glacier meltwater hydrochemistry. *Applied Geochemistry* 17, 855-883.

699 Cadene, A., Durand-Vidal, S., Turq, P., Brendle, J., 2005. Study of individual Na-
700 montmorillonite particles size, morphology, and apparent charge. *Journal of Colloid and*
701 *Interface Science* 285, 719-730.

702 Chang, Y.-I., Wang, M.-C., 2004. Heteroflocculation of equal numbers of different sized
703 colloidal particles in binary dispersions under enhanced gravity forces. *Colloids and Surfaces*
704 *A: Physicochemical and Engineering Aspects* 251, 75-86.

705 Czigány, S., Flury, M., Harsh, J.B., 2005. Colloid Stability in Vadose Zone Hanford
706 Sediments. *Environmental Science & Technology* 39, 1506-1512.

707 Darbha, G.K., Schäfer, T., Heberling, F., Lüttge, A., Fischer, C., 2010. Retention of Latex
708 Colloids on Calcite as a Function of Surface Roughness and Topography. *Langmuir* 26, 4743-
709 4752.

710 Ferrage, E., Lanson, B., Sakharov, B.A., Drits, V.A., 2005. Investigation of smectite
711 hydration properties by modeling experimental X-ray diffraction patterns: Part I.
712 Montmorillonite hydration properties. *Am. Miner.* 90, 1358-1374.

713 Filby, A., Plaschke, M., Geckeis, H., Fanghänel, T., 2008. Interaction of latex colloids with
714 mineral surfaces and Grimsel granodiorite. *Journal of Contaminant Hydrology* 102, 273-284.

715 Finck, N., Bouby, M., Dardenne, K., Geckeis, H., 2012. Characterization of Eu(III) co-
716 precipitated with and adsorbed on hectorite: from macroscopic crystallites to nanoparticles.
717 *Mineralogical Magazine* 76, 2723-2740.

718 French, R.A., Jacobson, A.R., Kim, B., Isley, S.L., Penn, R.L., Baveye, P.C., 2009. Influence
719 of Ionic Strength, pH, and Cation Valence on Aggregation Kinetics of Titanium Dioxide
720 Nanoparticles. *Environmental Science & Technology* 43, 1354-1359.

721 Furukawa, Y., Watkins, J.L., 2012. Effect of Organic Matter on the Flocculation of Colloidal
722 Montmorillonite: A Modeling Approach. *J. Coast. Res.* 28, 726-737.

723 Gallego-Urrea, J., Hammes, J., Cornelis, G., Hassellöv, M., 2014. Multimethod 3D
724 characterization of natural plate-like nanoparticles: shape effects on equivalent size
725 measurements. *J. Nanopart. Res.* 16, 1-17.

726 Gantenbein, D., Schoelkopf, J., Matthews, G.P., Gane, P.A.C., 2011. Determining the size
727 distribution-defined aspect ratio of platy particles. *Applied Clay Science* 53, 544-552.

728 Gao, S.A., Walker, W.J., Dahlgren, R.A., Bold, J., 1997. Simultaneous sorption of Cd, Cu,
729 Ni, Zn, Pb, and Cr on soils treated with sewage sludge supernatant. *Water Air and Soil*
730 *Pollution* 93, 331-345.

731 Gaucher, E.C., Tournassat, C., Pearson, F.J., Blanc, P., Crouzet, C., Lerouge, C., Altmann, S.,
732 2009. A robust model for pore-water chemistry of clayrock. *Geochim. Cosmochim. Acta* 73,
733 6470-6487.

734 Geckeis, H., Schäfer, T., Hauser, W., Rabung, T., Missana, T., Degueldre, C., Möri, A.,
735 Eikenberg, J., Fierz, T., Alexander, W.R., 2004. Results of the colloid and radionuclide
736 retention experiment (CRR) at the Grimsel Test Site (GTS), Switzerland – impact of reaction
737 kinetics and speciation on radionuclide migration. *Radiochim. Acta* 92, 765-774.

738 Gélinas, V., Vidal, D., 2010. Determination of particle shape distribution of clay using an
739 automated AFM image analysis method. *Powder Technology* 203, 254-264.

740 Hauser, W., Geckeis, H., Kim, J.I., Fierz, T., 2002. A mobile laser-induced breakdown
741 detection system and its application for the in situ-monitoring of colloid migration. *Colloids*
742 *and Surfaces A: Physicochemical and Engineering Aspects* 203, 37-45.

743 Holthoff, H., Egelhaaf, S.U., Borkovec, M., Schurtenberger, P., Sticher, H., 1996.
744 Coagulation Rate Measurements of Colloidal Particles by Simultaneous Static and Dynamic
745 Light Scattering. *Langmuir* 12, 5541-5549.

746 Hu, J., Xu, D., Chen, L., Wang, X.K., 2009. Characterization of MX-80 bentonite and its
747 sorption of radionickel in the presence of humic and fulvic acids. *J. Radioanal. Nucl. Chem.*
748 279, 701-708.

749 Huber, F., Enzmann, F., Wenka, A., Bouby, M., Dentz, M., Schäfer, T., 2012. Natural micro-
750 scale heterogeneity induced solute and nanoparticle retardation in fractured crystalline rock.
751 *Journal of Contaminant Hydrology* 133, 40-52.

752 Huber, F., Heck, S., Truche, L., Bouby, M., Brendlé, J., Höss, P., Schäfer, T., 2014.
753 Radionuclide desorption kinetics on synthetic Zn/Ni-labelled montmorillonite nanoparticles.
754 *Geochim. Cosmochim. Acta* Just accepted.

755 Jennings, B.R., 1993. Size and thickness measurement of polydisperse clay samples. *Clay*
756 *Minerals* 28, 485-494.

757 Jennings, B.R., Parslow, K., 1988. Particle Size Measurement: The Equivalent Spherical
758 Diameter. *Proceedings of the Royal Society of London. A. Mathematical and Physical*
759 *Sciences* 419, 137-149.

760 Jia, J., Iwata, S., 2010. Nonequilibrium structure of primary particles in colloidal bidispersion.
761 *Colloid Polym Sci* 288, 1485-1493.

762 Kammer, F.v.d., Baborowski, M., Friese, K., 2005. Field-flow fractionation coupled to multi-
763 angle laser light scattering detectors: Applicability and analytical benefits for the analysis of
764 environmental colloids. *Analytica Chimica Acta* 552, 166-174.

765 Karnland, O., Olsson, S., Nilsson, U., 2006. Mineralogy and sealing properties of various
766 bentonites and smectite-rich clay materials. SKB internal report TR-06-30.

767 Keiding, K., Nielsen, P.H., 1997. Desorption of organic macromolecules from activated
768 sludge: Effect of ionic composition. *Water Research* 31, 1665-1672.

769 Kretzschmar, R., Holthoff, H., Sticher, H., 1998. Influence of pH and Humic Acid on
770 Coagulation Kinetics of Kaolinite: A Dynamic Light Scattering Study. *Journal of Colloid and*
771 *Interface Science* 202, 95-103.

772 Kunkel, W.B., 1948. Magnitude and Character of Errors Produced by Shape Factors in
773 Stokes's Law Estimates of Particle Radius. *Journal of Applied Physics* 19, 1056-1058.

774 Lee, S.Z., Chang, L., Chen, C.M., Tsai, Y.I., Liu, M.C., 2001. Predicting soil-water partition
775 coefficients for Hg(II) from soil properties. *Water Science and Technology* 43, 187-196.

776 Liu, L., Moreno, L., Neretnieks, I., 2008. A Novel Approach to Determine the Critical
777 Coagulation Concentration of a Colloidal Dispersion with Plate-like Particles. *Langmuir* 25,
778 688-697.

779 Macdonald, D.D., Sharifi-Asl, S., 2011. Is Copper Immune to Corrosion When in Contact
780 With Water and Aqueous Solutions? Swedish Radiation Safety Authority, SSM, Report
781 2011:09.

782 Meier, L.P., Kahr, G., 1999. Determination of the cation exchange capacity (CEC) of clay
783 minerals using the complexes of copper(II) ion with triethylenetetramine and
784 tetraethylenepentamine. *Clay Clay Min.* 47, 386-388.

785 Meunier, A., 2005. *Clays*. Springer-Verlag Berlin Heidelberg.

786 Missana, T., Alonso, Ú., Turrero, M.J., 2003. Generation and stability of bentonite colloids at
787 the bentonite/granite interface of a deep geological radioactive waste repository. *Journal of*
788 *Contaminant Hydrology* 61, 17-31.

789 Möri, A., Alexander, W.R., Geckeis, H., Hauser, W., Schafer, T., Eikenberg, J., Fierz, T.,
790 Degueudre, C., Missana, T., 2003. The colloid and radionuclide retardation experiment at the

791 Grimsel Test Site: influence of bentonite colloids on radionuclide migration in a fractured
792 rock. *Colloids and Surfaces a-Physicochemical and Engineering Aspects* 217, 33-47.

793 Nakamaru, Y., Uchida, S., 2008. Distribution coefficients of tin in Japanese agricultural soils
794 and the factors affecting tin sorption behavior. *Journal of Environmental Radioactivity* 99,
795 1003-1010.

796 Norrfors, K.K., 2015. Stability and sorption capacity of montmorillonite colloids:
797 Investigation of size fractional differences and effects of γ -irradiation, KTH Applied Physical
798 Chemistry. KTH Royal Institute of Technology, Stockholm, Sweden.

799 Norrfors, K.K., Bouby, M., Marsac, R., Heck, S., Schäfer, T., Geckeis, H., Wold, S., 2015.
800 Montmorillonite colloids. II: The Dependency of Colloidal size on the Radionuclide Sorption
801 Capacities Manuscript in preparation.

802 Oliver, I.W., Merrington, G., McLaughlin, M.J., 2006. Copper partitioning among mineral
803 and organic fractions in biosolids. *Environmental Chemistry* 3, 48-52.

804 Oncsik, T., Trefalt, G., Csendes, Z., Szilagyi, I., Borkovec, M., 2014. Aggregation of
805 Negatively Charged Colloidal Particles in the Presence of Multivalent Cations. *Langmuir* 30,
806 733-741.

807 Ottewill, R.H., Shaw, J.N., 1966. Stability of monodisperse polystyrene latex dispersions of
808 various sizes. *Discussions of the Faraday Society* 42, 154-163.

809 Overbeek, J.T.G., 1980. The Rule of Schulze and Hardy. *Pure Appl. Chem.* 52, No. 5, 1151-
810 1161.

811 Pabst, W., Berthold, C., 2007. A Simple Approximate Formula for the Aspect Ratio of Oblate
812 Particles. *Particle & Particle Systems Characterization* 24, 458-463.

813 Pantina, J.P., Furst, E.M., 2006. Colloidal Aggregate Micromechanics in the Presence of
814 Divalent Ions. *Langmuir* 22, 5282-5288.

815 Perret, D., Newman, M.E., Nègre, J.-C., Chen, Y., Buffle, J., 1994. Submicron particles in the
816 rhine river—I. Physico-chemical characterization. *Water Research* 28, 91-106.

817 Plaschke, M., Schäfer, T., Bundschuh, T., Ngo Manh, T., Knopp, R., Geckeis, H., Kim, J.I.,
818 2001. Size Characterization of Bentonite Colloids by Different Methods. *Analytical*
819 *Chemistry* 73, 4338-4347.

820 Reerink, H., Overbeek, J.T.G., 1954. The rate of coagulation as a measure of the stability of
821 silver iodide sols. *Discussions of the Faraday Society*.

822 Schimpf, M., Caldwell, K., Giddings, J.C., 2000. *Field flow fractionation handbook*.

823 Schramm, L.L., Kwak, J.C.T., 1982a. Influence of exchangeable cation composition on the
824 size and shape of montmorillonite particles in dilute suspension. *Clay Clay Min.* 30, 40-48.

825 Schramm, L.L., Kwak, J.C.T., 1982b. Interactions in clay suspensions: The distribution of
826 ions in suspension and the influence of tactoid formation. *Colloids and Surfaces* 4, 43-60.

827 Schudel, M., Behrens, S.H., Holthoff, H., Kretzschmar, R., Borkovec, M., 1997. Absolute
828 Aggregation Rate Constants of Hematite Particles in Aqueous Suspensions: A Comparison of
829 Two Different Surface Morphologies. *Journal of Colloid and Interface Science* 196, 241-253.

830 Schäfer, T., Huber, F., Seher, H., Missana, T., Alonso, U., Kumke, M., Eidner, S., Claret, F.,
831 Enzmann, F., 2012. Nanoparticles and their influence on radionuclide mobility in deep
832 geological formations. *Applied Geochemistry* 27, 390-403.

833 Shah, P.S., Holmes, J.D., Johnston, K.P., Korgel, B.A., 2002. Size-selective dispersion of
834 dodecanethiol-coated nanocrystals in liquid and supercritical ethane by density tuning. *J.*
835 *Phys. Chem. B* 106, 2545-2551.

836 SKB, 2010. Design and production of the KBS-3 repository. SKB internal report TR-10-12.

837 Sposito, G., 1992. The diffuse-ion swarm near smectite particles suspended in 1:1 electrolyte
838 solutions: modified Gouy-Chapman theory and quasicrystal formation., in: Güven, N.,
839 Pollastro, R.M. (Eds.), *CMS Workshop Lectures 4, Clay water interface and its rheological*
840 *implications*. Clay minerals society, pp. 127-156.

841 Stumm, W., 1993. Aquatic colloids as chemical reactants: surface structure and reactivity.
842 *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 73, 1-18.

843 Tournassat, C., Bizi, M., Braibant, G., Crouzet, C., 2011. Influence of montmorillonite tactoid
844 size on Na–Ca cation exchange reactions. *Journal of Colloid and Interface Science* 364, 443-
845 454.

846 Tournassat, C., Neaman, A., Villiéras, F., Bosbach, D., Charlet, L., 2003. Nanomorphology of
847 montmorillonite particles: Estimation of the clay edge sorption site density by low-pressure
848 gas adsorption and AFM observations. *Am. Miner.* 88, 1989-1995.

849 Vahlund, F., Hermansson, H., 2006. A direct numerical approach to solving the transport
850 equations for radionuclide transport in fractured rock. SKB internal report R-04-50.

851 Weber, C., Heuser, M., Stanjek, H., 2014. A collection of aspect ratios of common clay
852 minerals determined from conductometric titrations. *Clay Minerals* 49, 495-498.

853 Veghte, D.P., Freedman, M.A., 2014. Facile Method for Determining the Aspect Ratios of
854 Mineral Dust Aerosol by Electron Microscopy. *Aerosol Science and Technology* 48, 715-724.

855 White, G.N., Zelazny, L.W., 1988. Analysis and implications of the edge structure of
856 dioctahedral phyllosilicates. *Clay Clay Min.* 36, 141-146.

857 Vieno, T., Ikonen, A.T.K., 2005. Plan for Safety Case of Spent Fuel Repository at Olkiluoto,
858 POSIVA Report 2005-1. POSIVA.

859 Wold, S., 2010. Sorption of prioritized elements on montmorillonite colloids and their
860 potential to transport radionuclides. SKB internal report TR-10-20.

861 Wolf, M., Buckau, G., Geyer, S., 2004. Isolation and characterisation of new batches of
862 GoHy-573 humic and fulvic acids., in: ed., G.B. (Ed.), *Humic substances in performance*
863 *assessment of nuclear waste disposal: Actinide and iodine migration in the far-field.*
864 *Wissenschaftliche Berichte FZKA 6969, Forschungszentrum Karlsruhe, pp. 111–124.*

865 Vuorinen, U., Snellman, M., 1998. Finnish reference waters for solubility, sorption and
866 diffusion studies Posiva Working Report 98-61 17-19.

867

868