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1 Porewater chemistry in compacted bentonite: application to the engineered 2 buffer barrier at the Olkiluoto site

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8 Abstract

9 Compacted bentonite is used as sealing and buffer material in engineered barrier systems (EBS) of high-
10 level radioactive waste repositories. The chemical characteristics of this clay and its porewater affect
11 the migration of radionuclides eventually released from the waste. They also determine the integrity
12 and long-term performance of the clay barriers. Key features are the structural negative charge and the
13 large proportion of structural (interlayer) water of the main mineral montmorillonite, which leads to
14 exclusion of anions and a surplus of cations in a large part of the porosity space. The objective of this
15 contribution was to assess the impact of different porosity model concepts on porewater chemistry in
16 compacted bentonite in the context of the planned Finnish spent nuclear fuel repository at Olkiluoto.
17 First, a structural model based on well-established crystallographic and electrostatic considerations was
18 set up to estimate the fractions of the different porosity types. In view of the uncertainty related to the
19 chemical properties of the interlayer water, two very different model concepts (anion-free interlayer,
20 Donnan space), together with a well-established thermodynamic model for bentonite, were applied to
21 derive the porewater composition of the bentonite buffer at Olkiluoto. The simulations indicate very
22 similar results in the “free” water composition for the two models and thus support the validity of the
23 reference porewater concept commonly used in performance assessment of waste repositories.
24 Differences between the models are evident in the composition of the water affected by the surface
25 charge (i.e. diffuse double layer and interlayer). These reflect the conceptual uncertainty in current
26 multi-porosity diffusion models.

27

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43 **Keywords:** bentonite, porewater chemistry, modelling, engineered barrier system, nuclear waste
44 repository

45 **1. Introduction**

46 Bentonite is used for many industrial and household applications. Owing to its plasticity, low
47 permeability and swelling capacity compacted bentonite is also used as seal, backfill and buffer for
48 nuclear waste repositories (Nagra 2002; Andra 2005; SKB 2011; Posiva 2013a). The main transport
49 process in this clay material is diffusion and therefore the movement of contaminants eventually
50 released from the waste is slow. The migration of many radionuclides and other solutes is affected by
51 the porewater chemistry in the bentonite which regulates their sorption and precipitation behaviour
52 (Ochs et al. 2004; Altmann 2008). In addition, the porewater chemistry in bentonite is an important
53 starting point to evaluate the impact of other components in the repository (e.g. cement, steel) on the
54 long term behaviour and performance of the buffer barrier (Posiva 2013a). The knowledge of the
55 porewater chemistry in this material, however, is still incomplete. This is related to the nanoporous
56 structure and the intimate clay-water association, which makes direct analysis of porewaters difficult
57 and may lead to alteration in porewater chemistry during the sampling and/or analytical procedure
58 (Sacchi et al. 2000).

59 A common approach to estimate the porewater composition in compacted bentonite has been
60 thermodynamic modelling (Wieland et al. 1994; Bruno et al. 1999; Curti & Wersin 2002; Bradbury &
61 Baeyens 2003; Wersin 2003; Wersin et al. 2004; Arcos et al. 2006), based on experimental data
62 obtained at low clay/water ratios (Snellman et al. 1987; Wanner et al. 1994; Ohe & Tsukamoto 1997;
63 Cuevas et al. 1997; Baeyens & Bradbury 1997; Muurinen & Lehtikoinen 1999; Bradbury & Baeyens 2002).
64 For example, Curti & Wersin (2002) could adequately describe the experimental data at different
65 clay/water ratios (0.015-1.5 kg/L) from Muurinen & Lehtikoinen (1999) with a simple thermodynamic
66 model. This model considers reactions at the clay surface including cation exchange occurring at
67 interlayer sites and pH-dependent protonation/deprotonation occurring at edge sites. Moreover,
68 equilibrium reactions with accessory minerals in the bentonite, such as gypsum, calcite, quartz and
69 kaolinite are included in the model. The modelling approaches in the studies mentioned above were
70 based on similar thermodynamic concepts.

71 An inherent uncertainty in these models is the extrapolation of the thermodynamic model validated at
72 low compaction degree to the compacted bentonite used for example as part of the engineered barrier
73 system for high-level radioactive waste repositories (Wersin 2003; Bradbury & Baeyens 2003). In
74 particular, the validity of electrostatic surface models (Tournassat et al. 2013) and the treatment of
75 interlayer water (Wersin et al. 2004; Wersin et al. 2014a) have been questioned. Some valuable
76 information in this regard has been obtained from experimental diffusion data. These data point to
77 lower accessible porosities for anions as compared to neutral species and cations (Kozaki et al. 2001;
78 Molera et al. 2003, Muurinen et al. 2007; Van Loon et al. 2007; Glaus et al. 2010). Based upon these
79 findings, anion-exclusion models have been formulated, which subdivide the water-filled pore space
80 into interlayer, diffuse (or electric) double layer (DDL) and "free" water porosities (Wersin et al. 2004;
81 Tournassat & Appelo 2011; Appelo 2013). In this formulation, anions are considered to reside in the
82 "free" electrically neutral solution and in the DDL in the external (intergranular) pores, whereas the
83 interlayer (intragranular) space is considered devoid of anions. Support for this model has been given by
84 molecular dynamics simulations (Rotenberg et al. 2007), but this issue remains controversial (Birgersson

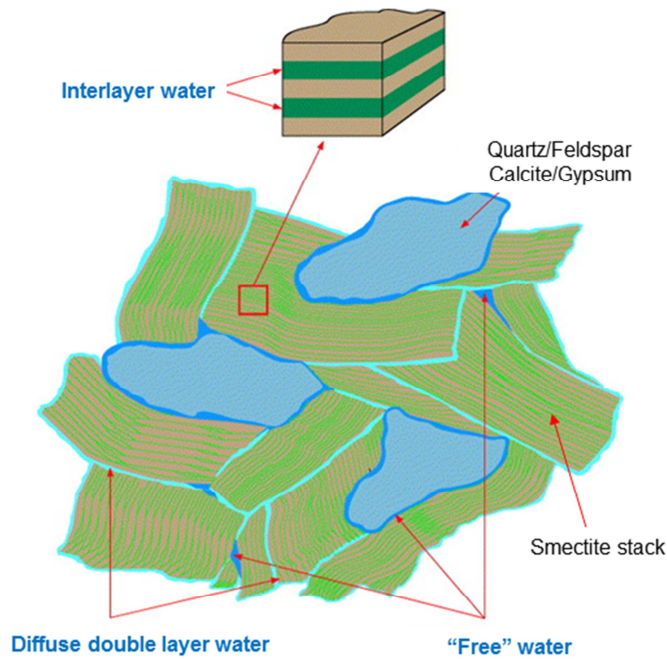
85 & Karnland 2009). Birgersson & Karnland (2009) postulated an osmotic model in which the entire
86 porespace is considered as Donnan space where both cations and anions reside. More recently, a
87 double porosity model including DDL and free water has been applied for describing simultaneous
88 cation and anion transport in bentonites (Alt-Epping et al. 2014; Tournassat & Steefel 2015). In this
89 model type, no difference is made between the interlayer and the external diffuse double layer and
90 anions can reside in this DDL space being only partially excluded by the negatively charged surface.

91 The general objective of this paper was to evaluate the different electrostatic and structural model
92 concepts for compacted bentonite and their effect on porewater chemistry. A further objective was to
93 test the robustness of porewater chemistry models for the bentonite buffer in the planned repository
94 site for spent fuel at Olkiluoto, Finland . In a first step, the geochemical model with two cases was set
95 up, based upon a well-established thermodynamic model approach (Wersin 2003; Curti & Wersin 2002;
96 Wersin et al. 2004) and more recent microstructural and electrostatic concepts (Tournassat & Appelo
97 2011; Tournassat & Steefel 2015). Second, the model was applied to the Olkiluoto site by considering six
98 different scenarios. Third, the results were compared and uncertainties highlighted in the light of the
99 performance of the bentonite barrier in geological repositories.

100 **2. Model description**

101 **2.1 Structural model**

102 Bentonite used as buffer material in geological repositories consists at least of 75% of montmorillonite
103 and accessory minerals, such as for example quartz, feldspar, illite, kaolinite, calcite and gypsum
104 (Bradbury et al. 2014; SKB 2011; Posiva 2013a). The micro/nano structure of bentonite is largely
105 determined by that of montmorillonite which may incorporate variable amounts of water in its
106 interlayer (IL), depending on the nature of the interlayer cation, the layer charge induced by isomorphic
107 substitution, ionic strength of the contacting solution, and montmorillonite mass per volume of water
108 (Tournassat & Appelo 2011). At the outer surfaces, an electric or diffuse double layer (DDL) develops
109 between the clay/water interface and the electrically neutral – “free” solution. Using these concepts the
110 porosity of saturated bentonite is thus represented by three water types IL, DDL and “free” as
111 schematically depicted in Fig. 1.



112
 113 *Fig. 1: Conceptual view of bentonite micro/nano structure and its porosity (modified from Bradbury &*
 114 *Baeyens 2003)*
 115

116 The relative proportions of the water types depend on various factors as outlined below, but because of
 117 uncertainties in microstructure and electrochemical properties vastly different models for porewater
 118 chemistry and solute diffusion have been proposed.

119 TOT layer and interlayer porosity:

120 The montmorillonite flakes are composed of negatively charged TOT layers alternating with 1-3 water
 121 layers containing charge compensating exchangeable cations (interlayers). The internal (basal) surface
 122 area of montmorillonite A_{int} (m^2/kg) can be calculated from the unit cell dimensions and the stacking
 123 number of TOT layers (Tournassat & Appelo 2011; Appelo 2013):

$$124 \quad A_{\text{int}} = 2 \frac{a \cdot b \cdot (n_c - 1)}{n_c} \frac{N_A}{MW} \quad (\text{m}^2/\text{g}) \quad (1)$$

125 where a (0.523 nm) and b (0.905 nm) are the unit lengths for montonclinic montmorillonite unit cell
 126 perpendicular to the c -axis, n_c is the stacking number in c direction, MW is the molecular weight of the
 127 montmorillonite and N_A is Avogadro's number ($6.022 \cdot 10^{23}$). The stacking number of TOT layers n_c in
 128 direction of the c axis depends on the type of interlayer cation (Pusch 2001, Melkior et al. 2009) and
 129 more generally on the preparation and experimental conditions (Muurinen et al. 2007, Tournassat &
 130 Appelo 2011), as discussed below. The molecular weight of montmorillonite purified from MX-80
 131 bentonite with the derived formula of $\text{Na}_{0.6}[\text{Si}_{7.92}\text{Al}_{0.08}][\text{Al}_{3.10}\text{Mg}_{0.48}\text{Fe}^{\text{III}}_{0.4}\text{Fe}^{\text{II}}_{0.02}]\text{O}_{20}\text{OH}_4$ (Madsen 1998) is
 132 745.2 g/mol, which is similar to the MW (745.4 g/mol) derived by Kiviranta & Kumpulainen (2011).
 133 Assuming that the edge surface area is small compared to the total surface area, the total specific
 134 surface area of montmorillonte (ssm) can be approximated to:

$$135 \quad ssm = 2a \cdot b \cdot \frac{N_A}{MW} \text{ (m}^2\text{/g)} \quad (2)$$

136 The derived value from the crystallographic parameters and the molecular mass of montmorillonite is
137 765 m²/g which is similar to that obtained by Madsen (1998) (749 m²/g).

138 The interlayer porosity in bentonite depends on the expansion of montmorillonite in contact with
139 water. This expansion in turns depends on the exchangeable cation, the ionic strength, the bentonite's
140 density, and density of the interlayer water. Based upon leaching and squeezing data, Muurinen et al.
141 (2007) proposed for Na-rich MX-80 bentonite a simple relationship between interlayer distance (h_{IL}) and
142 bentonite dry density (ρ_{dry}): $h_{IL} = 1.41 \cdot 10^{-9} - 4.9 \cdot 10^{-13} \cdot \rho_d$, thus ignoring the effect of ionic strength. Later,
143 Tournassat & Appelo (2011) derived the relation for Na-montmorillonite for the transition of 3 layer
144 hydrate to two layer hydrate, following Bourg et al. (2006) and using XRD data from Kozaki et al. (1998,
145 2008):

$$146 \quad h_{IL} = x_2 h_{IL}^{2WL} + x_3 h_{IL}^{3WL} \quad (3)$$

147 where x_2 and x_3 are the fractions of 2 layer hydrate and 3 layer hydrate, respectively with $x_2+x_3=1$. The
148 parameters h_{IL}^{2WL} (0.62 nm) and h_{IL}^{3WL} (0.94 nm) are the thicknesses of these hydrate layers. The fraction
149 x_2 varies between the montmorillonite dry density 1.3 kg/dm³ (minimum) and 1.6 kg/dm³ (maximum)
150 according to:

$$151 \quad x_2 = \frac{\rho_{d,m} - (1.3 - 3c_{free})}{1.6 - (1.3 - 3c_{free})} \quad (4)$$

152 where $\rho_{d,m}$ is the montmorillonite dry density in kg/dm³ and c is the concentration of NaCl in the "free"
153 external solution.

154 From the internal surface area A_{int} (m²/g) and the h_{IL} , the interlayer porosity in a compacted bentonite
155 can be calculated:

$$156 \quad \varepsilon_{IL} = \frac{A_{int}}{2} \cdot h_{IL} \cdot f_d \cdot w_{mm} \cdot \rho_d \quad (5)$$

157 where f_d is the density ratio of water in the interlayer and in the external pores and w_{mm} is the mass
158 fraction of montmorillonite. Assuming the same density of interlayer and external water ($f_d=1$)
159 (Tournassat & Appelo 2011) the interlayer porosity can be calculated from eqs. (2), (3) and (4).

160 Thus, the interlayer porosity is dependent on the bentonite density, the montmorillonite fraction, the
161 layer stacking number and the ionic strength. Application of eq. (5) shows that the amount of interlayer
162 porosity increases strongly with density and becomes a major porosity fraction above a density of 1.5
163 kg/dm³. Considering the buffer target dry density 1.57 kg/dm³ and a montmorillonite mass fraction of
164 0.75 in the Finnish concept (Posiva 2013a), then application of eq. (5) shows for a stacking number of 5
165 an interlayer porosity of 0.25 which is 53% of the total porosity. With a stacking number of 25 an
166 interlayer porosity of 0.29 is obtained corresponding to 62% of the total porosity. Note that at this
167 density the effect of ionic strength on interlayer porosity is small (within 1%).

168 Diffuse double layer (DDL) and "free" water porosities:

169 The external surface in montmorillonite consisting of basal and edge surfaces is influenced by the
 170 geometric configuration, thus the size and stacking number of the flakes. The average diameter of
 171 montmorillonite flakes is about 50–200 nm (Pusch 2001, Plaschke et al. 2001, Tournassat et al. 2003,
 172 Le Forestier et al. 2010), leading to a stacking number of about 200 in the a and b directions (Tournassat
 173 & Appelo 2011; Appelo 2013). Under these premisses, the contribution of the edges to the external
 174 surface (A_{ext}) can be neglected and:

$$175 \quad A_{\text{ext}} = 2 \frac{a \cdot b}{n_c} \frac{N_A}{MW} = \frac{ssm}{n_c} \text{ (m}^2\text{/g)} \quad (6)$$

176 The negatively charged surface is compensated by an excess of cations in the diffuse layer. The
 177 concentrations in the DDL contacting a “free” electrically neutral solution can be obtained from
 178 formulations based on the Poisson-Boltzmann equation. For example, the concentrations in the diffuse
 179 layer can be calculated by the method of Borkovec & Westall (1983), which explicitly integrates the
 180 Poisson-Boltzmann equation (e.g. Wersin et al. 2004). Alternatively, the ions in the DDL can be averaged
 181 by considering the Donnan approximation (Leroy et al. 2006; Appelo & Wersin 2007; Tournassat &
 182 Appelo 2011), as outlined below. The thickness of the DDL is commonly expressed by the Debye length
 183 (d_{DDL}) (Appelo 2013):

$$184 \quad d_{\text{DDL}} = \frac{3.09 \cdot 10^{-10}}{\sqrt{I}} f_{\text{DDL}} \text{ (m)} \quad (7)$$

185 where I is the ionic strength in the external pores and f_{DDL} is the number of Debye-lengths. The d_{DDL} has
 186 been shown to be difficult to constrain from experimental data in compact clays and f_{DDL} is often used as
 187 fitting parameter (Tournassat & Appelo 2011, Appelo 2013).

188 From the external surface area and the DDL thickness, the DDL porosity then becomes:

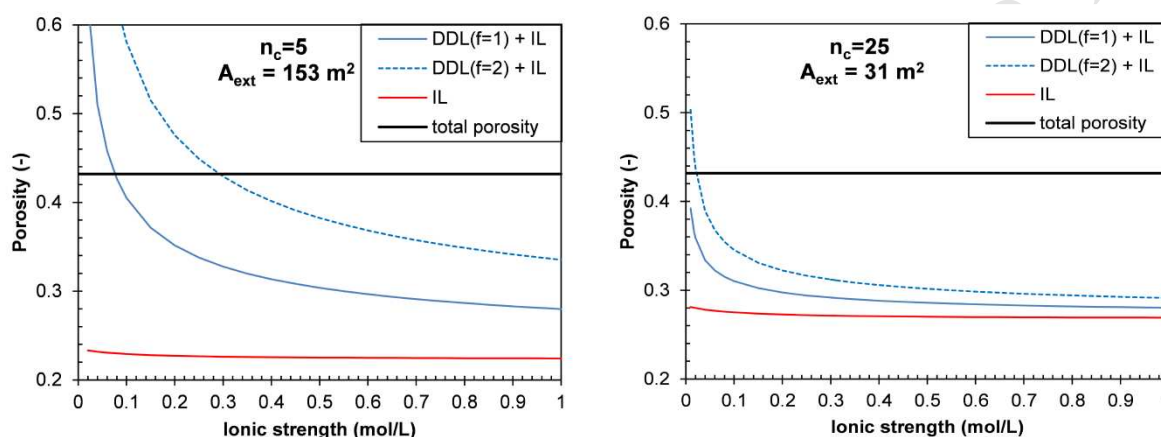
$$189 \quad \varepsilon_{\text{DDL}} = A_{\text{ext}} \cdot d_{\text{DDL}} \cdot w_{\text{mm}} \cdot \rho_d \quad (8)$$

190 The remaining porosity of the “free” solution is:

$$191 \quad \varepsilon_{\text{free}} = \varepsilon_{\text{tot}} - \varepsilon_{\text{IL}} - \varepsilon_{\text{DDL}} \quad (9)$$

192 Thus, from above equations the different porosity fractions for a given ionic strength can be derived if
 193 the stacking number n_c and the Debye length multiplier can be estimated. It is instructive to estimate
 194 the proportions of the different porosities for the bentonite buffer conditions and notably to evaluate
 195 the fraction of ε_{DDL} under different assumptions regarding n_c and f_{DDL} . The dependence of IL and DDL
 196 porosities as function of ionic strength for a bentonite dry density of 1.56 kg/dm^3 and $w_{\text{mm}} = 0.75$ is
 197 shown in Fig. 2. As pointed out above, the interlayer porosity shows only a very slight dependence on
 198 ionic strength and makes up about 52% and 62% of the total porosity for stacking numbers of 5 and 25,
 199 respectively. The effect of stacking number is much larger on the external DDL porosity. At low stacking
 200 number, thus high external surface area, the DDL porosity calculated from eq. (8) increases beyond the
 201 total porosity at lower ionic strength. This physically impossible result highlights the space constraints in
 202 the external pores of the compacted clay whose average thickness is in the same range as that of the
 203 interlayer. It also may suggest that a higher stacking number and thus a lower external surface area in
 204 the compacted clay should be considered. Support for a lower external surface in bentonite is provided

205 by BET measurements (Bradbury & Baeyens 2002) indicating an external surface area of $\sim 30 \text{ m}^2/\text{g}$. This
 206 value corresponds to a stacking number of ~ 25 in our simple structural model. On the other hand,
 207 HRTEM measurements on compacted MX-80 bentonite samples (Melkior et al. 2009) indicate somewhat
 208 lower numbers of TOT layers, ranging from 1-10 for Na-bentonite, 7-50 layers for Ca-bentonite and for
 209 ~ 15 layers for a bentonite contacted with a mixed electrolyte solution. Referring again to our simple
 210 structural model, lower stacking numbers with high external surface areas at lower ionic strength would
 211 imply 1-2 Debye lengths (Fig. 2). At ionic strengths below 0.1 mol/L, this would imply a Debye-length
 212 below 1, meaning that the DDL would be overlapping.



213
 214 *Fig. 2: Distribution of interlayer (IL) and diffuse double layer (DDL) porosity as function of ionic*
 215 *strength for different stacking numbers (n_c) and corresponding external surfaces areas (A_{ext}).*
 216 *Left: stacking number of 5. Right: stacking number of 25. Blue lines: sum of IL and DDL porosity*
 217 *with Debye length multiplier $f = 1$ (solid) and $f = 2$ (dashed). Red line: IL porosity.*
 218

219 From the above considerations, it appears that there are principally two parameters affecting the
 220 porosity distribution, which cannot be directly assessed, namely the stacking number n_c and the number
 221 of Debye lengths f_{DDL} . As discussed in Tournassat & Appelo (2011), diffusion data (see below) may help
 222 to bound the non-measurable parameters.

223 2.2 Estimates of model parameters based on diffusion data

224 There are different diffusion models for compacted bentonite, most of which, however are based upon
 225 the anion-exclusion and multi-porosity considerations (e.g. Leroy et al. 2006; Muurinen et al. 2007;
 226 Melkior et al. 2009; Tournassat & Appelo 2011; Alt-Epping et al. 2014). We also note the “single
 227 porosity” model of Birgersson & Karnland (2009) in which the entire porosity is lumped into one Donnan
 228 space. This latter model has been tested for simple NaCl electrolyte systems and, as discussed in
 229 Tournassat & Appelo (2011), appears to describe diffusion data adequately for a small range of
 230 bentonite densities, the details of which are not further discussed here.

231 Anion-free interlayer (AFI) models:

232 In these model types, the interlayer is considered to be devoid of anions and part of the crystallographic
 233 montmorillonite structure. Nevertheless, exchangeable cations may diffuse in this interlayer space as
 234 demonstrated by experimental data (e.g. Glaus et al. 2013).

235 Muurinen et al. (2007) equilibrated MX-80 bentonite samples at different densities ($0.5 - 1.5 \text{ kg}/\text{dm}^3$)
 236 with different NaCl solutions. They could adequately describe their chloride distribution by a double

237 porosity model including an anion-free interlayer and Donnan equilibrium between the external
 238 porosity and the external solution. An important parameter in their model was the external surface area
 239 which was taken to be either 20m²/g for all densities or varied from 15-140 m²/g from high to low
 240 densities.

241 Using anion-accessible porosity data of Muurinen (2006), Wersin et al. (2014a) conducted a preliminary
 242 fitting exercise based on an anion-free interlayer model described in Appelo (2013). Thereof, a stacking
 243 number of 4.8, a Debye length multiplier of 5.0 and an internal surface area of 487 m²/g were
 244 estimated.

245 A systematic evaluation of anion-accessible porosity data (Muurinen et al. 1989; 2004; 2007; Molera et
 246 al. 2003; Van Loon et al. 2007) was done by Tournassat & Appelo (2011). The large scatter in the data
 247 was highlighted, likely explained by different composition and preparation of samples as well as the
 248 measurement procedure. Nevertheless, fairly good agreement between experimental and modelled
 249 anion-accessible porosities could be obtained in the range of 0.1–0.4 M ionic strengths. Different
 250 models with different assumptions and parameter variation were tested. In general, best fits were
 251 obtained by varying the stacking number as function of density and reducing the interlayer space to one
 252 water layer at high densities. The authors explained their model result by changes in the microstructure
 253 as function of compaction and ionic strength.

254 Donnan space (DS) models:

255 In these models, the interlayer porosity and external DDL porosity are considered as single Donnan
 256 space (also termed microporosity) which is in osmotic equilibrium with “free” water (also termed
 257 macroporosity) (Alt-Epping et al. 2014; Tournassat & Steefel 2015). This assumption is equivalent to an
 258 assumed stacking number of 1. The negatively charged surface is compensated by a surplus of cations in
 259 this space according to the Donnan approximation in which the surface potentials and ion
 260 concentrations in the DDL are averaged according to:

$$261 \quad c_{D,i} = c_{free,i} \exp\left(\frac{-z_i F \psi_D}{RT}\right) \text{ (mol/L)} \quad (10)$$

262 where $C_{D,i}$ and $c_{free,i}$ is the concentration of species i in the Donnan space and the “free” solution,
 263 respectively, z_i is the charge of species i , and ψ_D is the Donnan potential. Note that a common
 264 approximation inherent in eq. (10) is to assume equal activity coefficients of the individual species in
 265 $C_{free,i}$ and $C_{D,i}$ which may not be the case (Appelo & Wersin 2007, Tournassat & Steefel 2015). The sum of
 266 ions in the Donnan space counterbalances the surface charge (q):

$$267 \quad \sum_i z_i c_{D,i} + q = 0 \text{ (mol/L)} \quad (11)$$

268 Thus, the Donnan potential is calculated from the condition imposed by eq. (11).

269 An advantage of DS models over AFI models (i.e. differentiating between an anion-free IL and an
 270 external DDL) is the fewer number of structural parameters required. For example, the porosity fraction
 271 of the Donnan space can be derived from double layer thickness according to eq. (7) and the total
 272 surface area of montmorillonite (Steefel et al. 2014). Due to the fact that the largest contribution stems
 273 from the interlayers with DDL thicknesses of 1-3 water layers the Debye length multiplier is commonly
 274 set to low values, i.e. ≤ 1 (Alt-Epping et al. 2014; Tournassat & Steefel 2015).

275 There is a rather fundamental difference how cation exchange is handled in the two model types: In the
276 AFI models the interlayer surface charge is completely screened by exchangeable cations, whereas this
277 is not the case in DS models. In fact, in most simple DS model no screening of the negative surface
278 charge is assumed, and cations are distributed between the free solution and the DDL according
279 Donnan equilibrium. Thus, the concentrations of cations in the Donnan space are governed by charge,
280 but not by chemical constraints. The selectivity of exchangeable cations, can however be considered by
281 partial screening of the surface with surface complexed (immobile) cations (Appelo & Wersin 2007;
282 Appelo et al. 2010; Alt-Epping et al. 2014).

283 The adequacy of DS model approach for describing anion-accessible porosity data has so far – to the
284 best of our knowledge- not been assessed in a systematic way. However, a few very recent modelling
285 studies have been carried out on experimental diffusion data. Tournassat & Steefel (2015) presented
286 two DS modelling exercises for simulating the experimental data of Tachi & Yotsuji (2014) and of Glaus
287 et al. (2013). In both cases partial screening of the surface charge by cations sorbed in the Stern layer
288 was assumed. The simulated breakthrough behaviour of the anionic (I⁻) and other tracers (HTO, ²²Na⁺,
289 ¹³⁷Cs⁺) showed a good match with the experimental data of Tachi & Yotsuji (2014) which involved ionic
290 strength of 0.1 M NaClO₄. In the case of the second dataset of Glaus et al. (2013) diffusion of ²²Na⁺
291 under salinity gradient in two diffusion experiments was modelled. An equally good match of the
292 experimental data could be achieved as with the AFI model applied by Glaus et al. (2013).

293 A benchmark modelling exercise involving different reactive transport simulators was performed by Alt-
294 Epping et al. (2014) on a flow-through column experiment for which an extensive chemical and
295 hydraulic dataset was available (Jenni et al. 2014). Besides more conventional model approaches, a DS
296 model with two porosity domains (Donnan and “free” solution) was applied using PHREEQC (Parkhurst
297 & Appelo 2013) and CrunchFlowMC (Steefel et al. 2014), which are so far the only reactive transport
298 simulators including the electrostatic effects in clays (Tournassat & Steefel 2014). Also, in this DS model,
299 partial screening of the surface charge by sorbed cations was assumed. A central result was that only
300 the DS model could simulate experimental breakthrough curves for major cations and anions
301 adequately.

302 In summary, the results highlight that multicomponent diffusion models including an electrostatic
303 description of the clay-water interface are required to properly simulate experimental diffusion data. It
304 appears that the two models (AFI and DS) involving two widely different assumptions regarding the
305 treatment of interlayer water adequately describe these experimental data.

306 **2.3 Setting up a geochemical model**

307 As is evident from the discussion in the previous sections, there are considerable uncertainties related
308 to microstructural and electrostatic properties of compacted bentonite in spite of the progress made in
309 the last years. Two cases representing implementations of the two conceptual models described above
310 and which are thought to encompass most of these uncertainties, will be considered: the first is based
311 upon the AFI triple porosity model concept and the second on the DF double porosity concept. The two
312 cases represent bounding cases with regard to the treatment of the montmorillonite surface charge and
313 of cation exchange: in the AFI model the major part of the surface (the internal surface) is screened by
314 sorbing (exchangeable) cations, whereas in the applied DS model the entire surface charge is
315 compensated in the DDL by the cation-enriched solution.

316 Both cases build on the well-established thermodynamic bentonite models (Wieland et al. 1994; Wersin
317 2003; Bradbury & Baeyens 2003) developed on the basis of experimental data at low compaction
318 (Wanner et al. 1992; Bradbury & Baeyens 1997; 2002; Muurinen & Lehtikoinen 1999). Reactions at the
319 montmorillonite surface include cation exchange and protonation/deprotonation via surface
320 complexation. The montmorillonite is otherwise considered to be inert, which is deemed justified in
321 view of the low solubility of this phase for the geochemical conditions considered (Wersin et al. 2014a).
322 However, the dissolution/precipitation of selected accessory minerals, such as gypsum, calcite, quartz
323 and kaolinite is included in the model.

324 AFI model:

325 This model is based on the approach presented in Wersin et al. (2004), but considers the
326 microstructural concept of montmorillonite presented above. The proportion of the porosity types, i.e.
327 IL, DDL and “free” are derived from the “crystallographic” specific montmorillonite surface area (765
328 m²/g) and an assumed fixed stacking number of 15 and a Debye length multiplier of 1. The stacking
329 number is an uncertain parameter, depending on a number of poorly constrained factors (see above).
330 The stacking number of 15 is deemed reasonable based on the microscopic observations of Melkior et
331 al. (2009) and moreover such a number leads to fairly high proportion of IL (eq. 4) as opposed to the DS
332 model. The selection of a Debye length multiplier of 1 for the DDL is based on the space considerations
333 (see above) and considerations of Tournassat & Appelo (2011). The diffuse double layer model of
334 Borkovec & Westall (1983) is applied which is implemented in PHREEQC and has been used in previous
335 studies (Curti & Wersin 2002; Wersin 2003; Wersin et al. 2004). The parameters for cation exchange and
336 surface complexation were also selected from those studies and are listed in Table 1.

337 DS model:

338 As outlined above, the IL and DDL are considered as a single Donnan space. The distribution of cations
339 and anions in the Donnan space and the “free” water is governed by Donnan equilibrium. It is assumed
340 that the activity ratio between the species concentration in the free and in the DDL is equal to one, as
341 implemented in PHREEQC v.3. A further assumption is that the full negative surface charge is
342 compensated by cations in the Donnan space, hence no screening of the surface charge by complexed
343 cations occurs.

344 Scoping calculations revealed that, owing to the high surface charge, the Donnan space becomes large
345 at lower ionic strength. Application of eq. (7) at high densities points to Debye lengths smaller than one,
346 thus to overlapping of the DDL. The extent of overlap, however, is difficult to constrain with our model
347 approach. The same feature has previously been noted when the DS was applied to high density clay
348 systems (e.g. Tournassat & Steefel 2015). Because of this difficulty and for better comparison of the two
349 models, we adapt the DDL length such that the proportion of “free” water in the DS model matches that
350 obtained for AFI model. As in the AFI model, the protonation/deprotonation at the external surface is
351 considered. The corresponding parameters are presented in Table 1.

352

353 **Table 1** Parameters used for geochemical bentonite model. AFI (anion-free interlayer) and DS (Donnan
 354 space) represent two model variants as discussed in the text.

	Unit	AFI model	DS model	Comment
Structural parameters				
Specific montmorillon. surface area	m ² /g	765	765	see text
TOT stacking number		15	1	"
DDL length multiplier		1	<1,variable	see text
Montmorillonite mass fraction		0.75	0.75	"
DDL parameters				
Model used for diffuse layer		DDL*	Donnan	DDL*: Borkovec & Westall 1983
Considered porosity		external	int.+ext.	
Cation exchange parameters				
CEC	eq/kg	0.787	0.787	Bradbury & Baeyens 2002
Initial occupancies	equiv. fraction	Na 0.848 Ca 0.084 Mg 0.051 K 0.017		Bradbury & Baeyens 2002
logK _{Na/Ca}		0.41		Gaines-Thomas convention used for cation exchange model
logK _{Na/Mg}		0.31		"
logK _{Na/K}		0.60		"
Surface complexation parameters				
Surface site concentration	eq/kg	0.0284	0.0284	Wieland et al. 1994
Surface area	m ² /g	31.5	31.5	Bradbury & Baeyens 2002
logK: ≡SOH + H ⁺ = ≡SOH ₂ ⁺		5.4	5.4	Wieland et al. 1994
logK: ≡SOH = ≡SO ⁻ + H ⁺		-6.7	-6.7	"
Dissolution of accessories / inventories				
NaCl	mol/kg	1.35E-03	1.35E-03	Bradbury & Baeyens 2002, complete dissolution
Gypsum ¹	mol/kg	0.0235	0.0235	Bradbury & Baeyens 2002
CaSO ₄ ·2H ₂ O ↔ Ca ²⁺ + SO ₄ ²⁻ + 2H ₂ O	logK	-4.61	-4.61	Giffaut et al. 2014
Calcite ¹	wt%	0.7	0.7	Madsen 1998
CaCO ₃ ↔ Ca ²⁺ + CO ₃ ²⁻	logK	-8.48	-8.48	Giffaut et al. 2014
Quartz ¹	wt%	10–15	10–15	Madsen 1998
SiO ₂ + 2H ₂ O ↔ H ₄ SiO ₄	logK	-3.74	-3.74	Giffaut et al. 2014
Kaolinite ¹	wt%	Traces	Traces	Madsen 1998
Al ₂ Si ₂ O ₅ (OH) ₄ + 6H ⁺ ↔ 2Al ³⁺ + H ₄ SiO ₄ + H ₂ O	logK	6.51	6.51	Giffaut et al. 2014

355 ¹ excess of these minerals assumed in all calculations

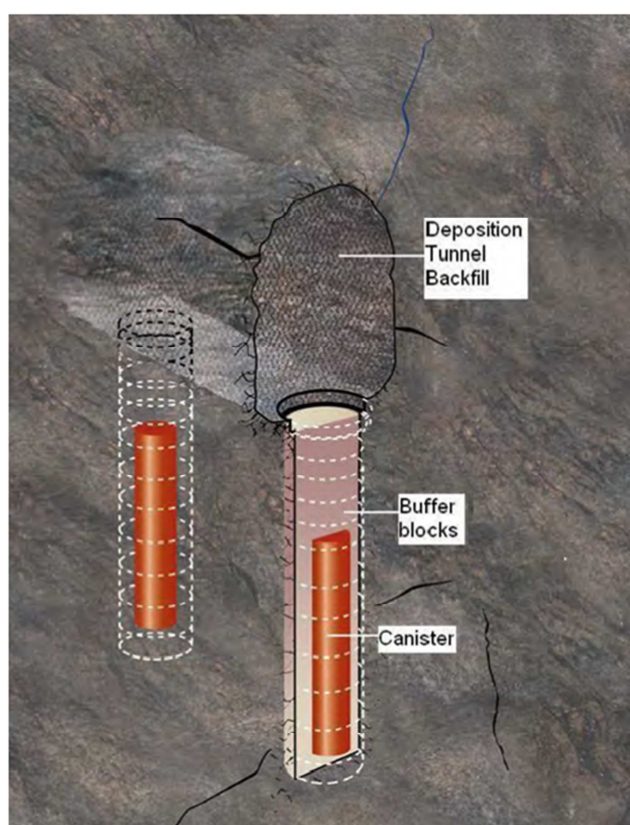
356 3. Application to the bentonite buffer at the Olkiluoto site

357 3.1 The bentonite buffer and groundwater chemistry

358 The engineered barrier system (EBS) for spent fuel waste at Olkiluoto is based on the KBS-3 disposal
 359 concept (Posiva 2013a): Waste containing copper canisters, surrounded by partially saturated
 360 compacted bentonite blocks (buffer), are emplaced in vertical deposition holes (Fig . 3), spaced at 10 m

361 at about 400 m depth below surface. The deposition holes and the overlying deposition tunnel are
 362 surrounded by variably fractured gneissic host rock.

363 The target density of the buffer is 2.0 kg/dm^3 at full saturation, thus corresponding to a dry density of
 364 1.57 kg/dm^3 . The reference buffer material is MX-80 Na-rich bentonite, but alternative bentonites with
 365 similar sealing properties are also being considered (Juvankoski et al. 2012). According to the disposal
 366 concept, after repository closure, saturation and swelling of the bentonite buffer will proceed via slow
 367 groundwater inflow from the host rock. Saturation times are expected to be variable and controlled on
 368 the one hand by the rate of water inflow and on the other by coupled thermo-hydro-mechanical
 369 behaviour in the buffer which is affected by elevated temperatures in the contacting canister (Posiva
 370 2013a). Thus, saturation times will vary and have been estimated to be in the range of decades to
 371 several hundreds of years (Posiva 2013a). Upon saturation, hydromechanical conditions will become
 372 more stable, due to the low hydraulic conductivity ($\sim 10^{-13}$ – 10^{-14} m/s) and high swelling pressure (6–8
 373 MPa) (Karnland et al. 2006) and slow diffusive transport will dominate.



374
 375 *Fig. 3: Schematic view of KBS-3 repository components (Posiva 2012). Of interest here are the*
 376 *bentonite buffer blocks surrounding the canister.*
 377

378 The groundwater composition at repository depth is fairly saline, Na-Cl dominated with a ionic strength
 379 of $\sim 0.2 \text{ M}$ and total dissolved solids (TDS) of $\sim 10 \text{ g/L}$ (Table 2). Due to continuing land uplift and climatic
 380 changes, the groundwater at repository level is predicted to become more dilute and more influenced
 381 by shallower brackish groundwaters with time (Posiva 2013a). Depending on the conditions, it has been
 382 envisioned that very dilute groundwaters could reach repository levels during the next glaciation (Posiva
 383 2013a). On the basis of the expected hydrochemical evolution reference groundwaters have been

384 defined (Hellä et al. 2014). These serve to bound the range of groundwater composition in contact with
385 the bentonite buffer. For that purpose, specific groundwater compositions based on samples from deep
386 boreholes were derived, assuming calcite and quartz equilibrium at 25 °C. Table 2 depicts two reference
387 groundwaters in the "groundwater" columns: a saline type, representing present conditions at
388 repository levels and a dilute type representing a bounding groundwater composition.

389 **3.2 Defining initial conditions**

390 The purpose here is to define the initial geochemical conditions in the bentonite buffer (Curti & Wersin
391 2002). Here we assume that in the beginning of the analysis the buffer is fully saturated and that the
392 thermal pulse arising from the decay of short lived nuclides in the waste has dissipated. We consider
393 diffusive equilibration between bentonite porewater and the surrounding groundwater, but also a case
394 is considered in which groundwater is instantaneously admixed with the bentonite buffer.

395 In a first step, the composition of the initial porewater for all cases was defined, following the procedure
396 proposed in Wersin et al. (2004). The initial exchanger composition and accessory minerals (calcite,
397 gypsum, quartz and kaolinite) and the external surface were equilibrated with a solution containing
398 NaCl according to its inventory in the bentonite (Table 1) under a partial pressure of CO₂ (pCO₂)
399 corresponding to atmospheric conditions (10^{-3.44} bar). This resulting surface and porewater composition
400 was then equilibrated with the surrounding groundwater as outlined in the following section.

401 The impact of selecting different initial conditions, such as different pCO₂, different exchanger
402 composition or NaCl concentration, on the results was also tested (section 3.4).

403 Table 2 Concentrations of selected constituents in groundwater and calculated “free” porewater (pw) in mmol/kg_w for saline and dilute case.
 404 SI: saturation index; diff. eq.: diffusive equilibration; mixing: mixing assumption (see text).

	Saline case				Dilute case			
	groundwater	“free” porewater			groundwater	“free” porewater		
Model type Constraint		DS diff. eq.	AFI diff. eq.	AFI mixing		DS diff. eq.	AFI diff. eq.	AFI mixing
Ionic strength	215.1	243.2	242.5	454.1	18.9	91.9	94.8	95.5
pH	7.27	7.25	7.27	7.10	7.49	7.15	7.16	7.16
Alkalinity ¹	0.63	0.61	0.63	0.51	4.27	2.32	2.33	2.32
Na	116.1	122.4	131.3	213.9	13.2	33.8	36.1	36.5
K	0.28	0.31	0.32	0.50	0.25	0.70	0.65	0.65
Mg	2.6	3.2	3.4	8.2	0.7	7.4	7.8	7.9
Ca	32.8	42.2	38.8	84.8	1.2	12.8	12.7	12.8
Cl	182.5	182.5	182.5	368.5	9.9	9.9	9.9	11.4
CO ₃ (tot)	0.66	0.64	0.66	0.53	4.50	2.56	2.58	2.56
SO ₄	0.21	15.1	16.3	11.0	1.0	31.5	32.7	32.4
Si	0.17	0.17	0.17	0.16	0.18	0.18	0.18	0.18
log(pCO ₂)	-2.86	-2.86	-2.86	-2.86	-2.11	-2.11	-2.11	-2.11
SI calcite	0	0	0	0	0	0	0	0
SI gypsum	-1.88	0	0	0	-1.90	0	0	0
SI quartz	0	0	0	0	0	0	0	0

405 ¹ [Alk] = [HCO₃⁻]_T + 2[CO₃²⁻]_T where subscript T refers to the total concentration of HCO₃⁻ and CO₃²⁻, respectively

406 3.3 Definition and implementation of scenarios

407 The goal of the modelling exercise was to compare the compositions for the different water types
 408 (IL, DDL and “free”) obtained from the AFI and DS model. The buffer which had been pre-
 409 equilibrated according to section 3.3 was diffusively equilibrated separately with saline and a dilute
 410 external groundwater. This led to four scenarios to be assessed. In addition, for the AFI model a
 411 variant was considered in which the (pre-equilibrated) bentonite buffer was (instantaneously)
 412 admixed with saline groundwater (Wersin et al. 2004, Wersin et al. 2014a). With regard to cation
 413 exchange, it was further assumed that the exchanger composition in the AFI model is controlled by
 414 that of the external “free” porewater. In this way, the results can be readily compared with the DS
 415 model, although we are aware that equilibration of the exchanger may take a long time (Neretnieks
 416 et al. 2009). The six scenarios assessed are shown in Table 3.

417 The accessory minerals were assumed to be present excess in the buffer in all calculations. In the
 418 case of gypsum, which is fairly soluble, complete dissolution might be expected with time in view of
 419 the undersaturated conditions with respect to this phase in the crystalline groundwater. On the
 420 basis of hydraulic data and reactive transport modelling, it has been shown (Wersin et al. 2014b),
 421 however, that the gypsum is expected to persist for long timescales.

422

423 *Table 3: Model scenarios for deriving porewater composition of bentonite buffer. Fractions of*
 424 *different porosity types (IL: interlayer; DDL: diffuse double layer, “free”) also shown (see*
 425 *text)*

Model scenario	Model approach	Contacting groundwater	Assumption for chloride	% IL	%DDL	%“free”
AFI_saline_a	AFI	Saline type	$[Cl]_{free} = [Cl]_{gw}$	61.1	7.7	31.2
AFI_saline_b	AFI	Saline type	Mixing model	61.1	7.7	31.2
AFI_dilute_a	AFI	Dilute type	$[Cl]_{free} = [Cl]_{gw}$	63.1	32.6	4.3
AFI_dilute_b	AFI	Dilute type	Mixing model	63.1	32.6	4.3
DS_saline	DS	Saline type	$[Cl]_{free} = [Cl]_{gw}$	0	78.8	31.2
DS_dilute	DS	Dilute type	$[Cl]_{free} = [Cl]_{gw}$	0	95.7	4.3

426 AFI: anion-free interlayer; DS: Donnan space

427 Calculation of porosity distributions:

428 This calculation of the porosity distribution for the AFI model is straightforward based on the
 429 assumptions and the structural model detailed in sections 2.3 and 2.1, respectively. The derived
 430 proportions for IL, DDL and “free” water are shown in Table 3. As expected, the proportion of “free”
 431 water in the external porespace decreases with decreasing ionic strength, whereas that of the DDL
 432 increases. For the DS model, the proportions are derived as outlined in section 2.3.

433 Implementation in PHREEQC:

434 Calculations were based on the thermodynamic equilibrium model outlined in section 2.3. The
 435 thermodynamic database THERMOCHEMIE Version 9 (Giffaut et al. 2014) was applied and a
 436 temperature of 25 °C was assumed throughout which is somewhat above the reference temperature
 437 (~12 °C) in the surrounding rock. The reasons for selecting 25 °C for the calculations were: (i) the

438 minimisation of data uncertainties by using standard state conditions and (ii) the small differences in
439 the results expected from the temperature effect.

440 The groundwater solution was equilibrated with the pre-equilibrated bentonite considering cation
441 exchange and surface complexation reactions, as well as the dissolution / precipitation of accessory
442 minerals according to the premises outlined in Table 1. For the diffusive equilibration scenarios, the
443 anions concentrations in the “free” porewater were fixed to that in the groundwater by addition of
444 small amounts of NaCl and NaBr.

445 **3.4 Results**

446 The modelled data with the full composition is presented in the Supplementary data (Table SD-1).
447 Table 2 shows selected results for the “free” porewater compositions and compares these with the
448 corresponding groundwater data. A conspicuous feature is the similarity of the AFI and DS model
449 results, which a priori was not expected in view of the very distinct model assumptions with regard
450 to constraints for cations. This holds for the assessment scenarios in which diffusive equilibration
451 between groundwater and porewater is assumed. Changing the initial porewater and exchanger
452 composition (section 3.3.) resulted in only a marginal influence on the final compositions.

453 The differences between the “free” porewater and groundwater compositions are also fairly small
454 for the assessment scenarios assuming diffusive equilibration. The main difference arises from the
455 gypsum equilibrium in the buffer, leading to higher sulphate and calcium levels in the “free”
456 porewater.

457 The assumption of instantaneous mixing of groundwater with the bentonite buffer, leads to a higher
458 ionic strength in the saline case because of anion exclusion in the interlayer and the consequent
459 concentration of solutes in the external pores and different composition in the “free” porewater. For
460 the dilute case, however, this concentration effect is largely outcompeted by the large proportion of
461 DDL relative to “free” pore space (Table 4).

462 The concentrations of the main constituents in the DDL and the composition of exchangeable
463 cations are shown in Table 4 (in mmol per kg DDL water and per kg interlayer water). Obviously,
464 owing to the assumptions inherent in the two models, there are large differences in the cation
465 concentrations in the different compartments. In the AFI model the internal negative surface charge
466 is entirely compensated by exchangeable cations, whereas in the DS model the charge
467 compensation occurs entirely in the diffuse layer (Donnan) space. The proportions of Na, Ca and Mg
468 in the exchange complex in the AFI model and those in DDL in the DS model are slightly different,
469 where the Ca/Na and Mg/Na ratios are higher in the DS model (Table 4; see Discussion section).

470 **Table 4** Concentrations of selected constituents in mmol/kg DDL water and mmol/kg IL water,
 471 >S- represents surface complexation sites

Model Constraint	Saline case			Dilute case		
	DS diffusive eq.	AFI diffusive eq.	AFI mixing	DS diffusive eq.	AFI diffusive eq.	AFI mixing
DDL						
% total porosity	68.8%	7.7%	7.7%	95.7%	32.6%	32.6%
Na	778.0	286.8	317.8	322.6	51.0	51.2
K	1.96	0.71	0.75	6.75	0.92	0.93
Mg	118.5	15.4	19.9	515.4	17.1	17.2
Ca	1632.5	178.5	216.6	840.0	26.8	26.9
Cl	39.7	11.4	151.8	1.6	5.0	5.7
C	1.20	0.23	0.35	1.78	1.49	1.49
S	10.6	0.4	5.2	8.0	14.1	14.1
>S-OH	74.5	628.9	654.8	42.8	155.4	153.8
>S-O ⁻	72.8	692.9	662.1	61.4	113.4	115.3
>S-OH ₂ ⁺	3.8	28.6	32.5	42.8	10.7	10.3
Interlayer (IL)						
% total porosity	0%	61.0%	61.0%	0%	63.1%	63.1%
NaX		1995.2	2100.0		1000.2	978.8
CaX ₂		1257.7	1208.2		1152.4	1125.3
MgX ₂		89.3	86.8		640.7	626.6
KX		19.6	19.7		72.3	70.7

472

473 The concentrations of anions (Cl, SO₄) in the diffuse layer are lower compared to the “free” water
 474 because of the effect of the negative surface charge. They are also affected by the ionic strength,
 475 thus decreased in the dilute case.

476 3.5 Discussion

477 Application of “reference porewater” concept:

478 The derivation of so-called reference porewaters of the bentonite buffer based on thermodynamic
 479 modelling is a common approach in safety assessment of high-level waste repositories (Curti &
 480 Wersin 2002; Arcos et al. 2006; Bradbury et al. 2014; Wersin et al. 2014a). The compositions of these
 481 waters provide the basis for a number of processes considered in safety assessment, such as for
 482 example corrosion of the copper canister (Posiva 2013a). They also are used to derive retention
 483 parameters for radionuclides, such as solubilities and sorption values. These parameters are
 484 subsequently implemented in radionuclide transport calculations with simple diffusion models
 485 (Altmann 2008; SKB 2010; Posiva 2013b). The diffusion of radionuclides through the bentonite buffer
 486 is particularly affected by pH and complexing ligands such as carbonate and, to lesser extent,
 487 sulphate and chloride (Tachi et al. 2014, Wersin et al. 2014a). Thus, the robustness of the
 488 geochemical model and the uncertainties of the derived porewater composition play an important
 489 role in safety assessment. The results presented here suggest that uncertainties related to the
 490 electrostatic properties and description of different porosities of the bentonite do not have a large
 491 effect on the porewater chemistry. Notably, two largely different descriptions of the interlayer and
 492 diffuse double layer yield very similar results in the “free” porewater composition. This can be
 493 explained by the large chemical buffering capacity of the bentonite buffer, owing to its large cation

494 and proton exchange capacity and the presence of reactive accessory minerals, such as gypsum and
495 calcite.

496 Larger differences arise when equilibration between the porewater and surrounding groundwater is
497 based on the mixing assumption rather than by diffusive equilibration (see above). The mixing
498 assumption (i.e. instantaneous admixing of the groundwater with the bentonite buffer material) may
499 be appropriate for approximating transient conditions, such as during buffer saturation (Sena et al.
500 2010, Jenni et al. 2014). For longer time periods, the assumption of diffusive equilibration is
501 considered to be more appropriate (Posiva 2013b). From a safety assessment viewpoint, the
502 differences between these two model scenarios are not very relevant with regard to the mobility of
503 radionuclides in the buffer. This is indicated by the fairly similar solubilities and sorption values of RN
504 derived for reference porewaters with the diffusive equilibration and the mixing assumption,
505 respectively (Wersin et al. 2014a).

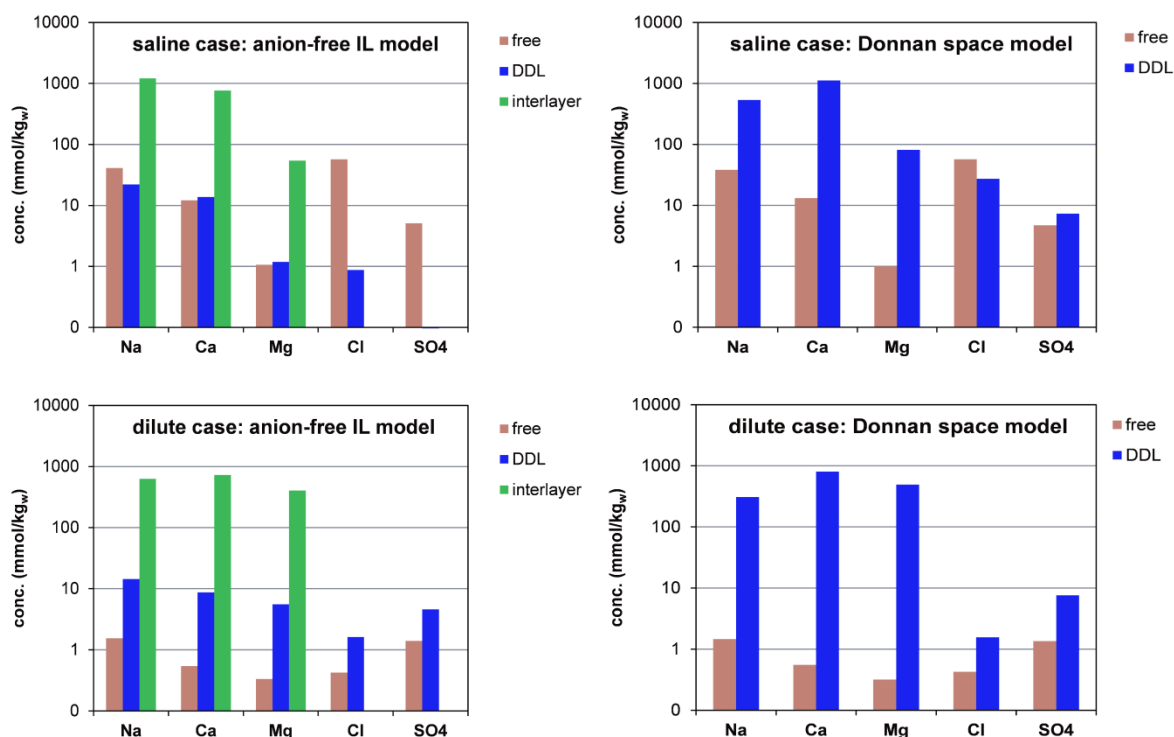
506 Basis for multicomponent diffusion modelling:

507 As outlined in section 2.2, multicomponent diffusion through compacted bentonite has been
508 successfully described by the AFI and DS model approaches. Also for this reason, the derivation of
509 porewater compositions presented above is based upon these approaches. The proportions in the
510 “free”, DDL and interlayer normalised per volume of total water illustrate the predominance of the
511 cation load in the interlayer (AFI model) and Donnan space (DS model), respectively (Fig. 4). This
512 reflects the large difference with regard to surface charge shielding inherent in the two approaches
513 (see above). It should be noted that in the DS model there is the possibility to shield a part of the
514 surface charge by fixing cations in the Stern layer (Tournassat & Steefel 2015) and thus diminishing
515 the cation load in the Donnan layer. The attributed fractions of cations in these two layers seem,
516 however, to be an arbitrary choice in view of the lack of theoretical or experimental basis (Alt-Epping
517 et al. 2014; Tournassat & Appelo 2015).

518 The effect of anion exclusion is mirrored by the chloride concentrations in the different porosities
519 (Fig. 4). In the saline case, the main chloride load predicted by the AFI model is in the “free” porosity
520 and only a minor fraction occurs in the diffuse layer. The DS model, on the other hand, predicts
521 similar chloride loads in both porosity spaces. In other words, the DS model predicts somewhat
522 higher Cl^- concentrations and thus also higher diffusive fluxes in the DS model relative to the AFI
523 model. In the dilute case, both models yield fairly similar results and higher Cl^- loads in the diffuse
524 layer compared to the “free” porosity space.

525 The different approaches used for describing the DDL in the AFI and DS models, i.e. the Gouy-
526 Chapman based model of Borkovec & Westall (1983) and the Donnan approximation, respectively,
527 yield very similar results in terms of composition in the DDL (not shown). This is because both
528 approaches are based on similar equations, as shown for example in Tournassat & Steefel (2015).

529



530
531 *Fig. 4: Concentrations (mmol/kg of total water) of selected constituents in different porosity*
532 *compartments: upper: saline case; lower: dilute case*
533

534 Conceptual issues:

535 In view of the considerable uncertainty regarding the porewater chemistry in the interlayer two
536 distinct model descriptions (anion-free, Donnan space) have been applied. In the Donnan space
537 model, the activity coefficients of species in the diffuse layer are commonly assumed to be the same
538 as in the “free” porewater (Appelo et al. 2010; Steefel et al. 2014). This assumption is questionable,
539 in particular for cations whose concentrations are in molar range. Activities may be affected by the
540 high surface charge (Tournassat & Appelo 2015), ion pair formation (Charlet & Tournassat 2005;
541 Bourg & Sposito 2011) and the decreased dielectric constant of water (Teschke et al. 2001). The
542 activity of divalent cations Ca^{2+} and Mg^{2+} is expected to be more influenced than that of Na^+ (Ferrage
543 et al. 2005), thus diminishing their selectivity in the diffuse layer.

544 Diffusive equilibration between the external groundwater and the buffer porewater is deemed to be
545 reasonable assumption when long timescales are considered. The time scale for diffusive mixing was
546 estimated from diffusion calculations to be a few hundreds to a few thousands of years (Wersin et
547 al. 2014b) whereas the period for evaluating repository safety comprises 10^5 to 10^6 years.

548 During transient conditions, the choice of model and the treatment of interlayer water will affect the
549 evolution of porewater chemistry and the time when equilibrium will be reached, as indicated by the
550 different chloride inventories (see above). This will be assessed in a subsequent contribution (Wersin
551 et al., in prep.).

552 On a more general level, the estimation of the different porosity fractions is based upon simplified
553 crystallographic and geometrical considerations neglecting the heterogeneous micro/nano
554 structure. Thus, layer collapse or the presence of gel-type domains (Tournassat & Appelo 2011,

555 Pusch 2001; Keller et al. 2014). With regard to the porewater chemistry, such features are not
556 expected to lead to strong effects. The two models representing widely different descriptions of the
557 porosity are thought to represent bounding cases encompassing the different structural
558 configurations.

559 **4. Conclusions**

560 A structural model based upon simple crystallographic and electrostatic principles has been set up to
561 derive the different porosity types in compacted bentonite. In view of the uncertainty related to the
562 chemical properties of the interlayer water two differing model concepts (anion-free interlayer,
563 Donnan space) together with a well-established thermodynamic model for bentonite were applied
564 to derive the porewater composition of the bentonite buffer for the Finnish nuclear repository site.
565 The simulations indicate very similar results in the “free” water composition for the two models
566 under the assumption of diffusive equilibration between the porewater and the surrounding
567 groundwater of the host rock. This result supports the validity of the reference porewater concept in
568 safety assessment as basis for deriving radionuclide solubility and sorption parameters. It also
569 indicates that the conceptual model uncertainties related to the microstructure of compacted
570 bentonite have a minor effect on its “free” porewater composition.

571 Due to the different assumptions inherent in the two models larger differences arise in the
572 simulated composition of the water affected by the negative surface charge. This is expected to have
573 consequences in the modelling of the transient porewater chemistry evolution. Further
574 experimental evidence is required to decide which type of multi porosity diffusion model is more
575 appropriate for describing this transient evolution.

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Highlights

- The porewater chemistry in bentonite was constrained by geochemical modelling
- Two very different interlayer model concepts yielded similar porewater compositions
- The results indicate the validity of the widely used reference porewater concept
- Differences between the models are evident in the diffuse double layer composition