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Porewater chemistry in compacted bentonite: Application to the engineered buffer barrier at the Olkiluoto site

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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
- similar results in the "free" water composition for the two models and thus support the validity of the
- 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
- charge (i.e. diffuse double layer and interlayer). These reflect the conceptual uncertainty in currentmulti-porosity diffusion models.
- 27

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- 42
- Keywords: bentonite, porewater chemistry, modelling, engineered barrier system, nuclear waste
 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 nuclear waste repositories (Nagra 2002; Andra 2005; SKB 2011; Posiva 2013a). The main transport 48 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 & Lehikoinen 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 & Lehikoinen (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,
- equilibrium reactions with accessory minerals in the bentonite, such as gypsum, calcite, quartz and
 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
- 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
- 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
- test the robustness of porewater chemistry models for the bentonite buffer in the planned repository
- site for spent fuel at Olkiluoto, Finland . In a first step, the geochemical model with two cases was set
- 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
- 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
- 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
- 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
- schematically depicted in Fig. 1.



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

115

112

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} (m²/kg) can be calculated from the unit cell dimensions and the stacking

123 number of TOT layers (Tournassat & Appelo 2011; Appelo 2013):

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

where a (0.523 nm) and b (0.905 nm) are the unit lengths for montonclinic montmorillonite unit cell perpendicular to the c-axis, n_c is the stacking number in c direction, MW is the molecular weight of the montmorillonite and N_A is Avogadro's number (6.022·10²³). The stacking number of TOT layers n_c in

- direction of the c axis depends on the type of interlayer cation (Pusch 2001, Melkior et al. 2009) and
- 129 more generally on the prepraration and experimental conditions (Muurinen et al. 2007, Tournassat &
- Appelo 2011), as discussed below. The molecular weight of montmorillonite purified from MX-80
- 131 bentonite with the derived formula of $Na_{0.6}[Si_{7.92}AI_{0.08}][AI_{3.10}Mg_{0.48}Fe^{III}_{0.04}Fe^{II}_{0.02}]O_{20}OH_4$ (Madsen 1998) is
- 132 745.2 g/mol, which is similar to the MW (745.4 g/mol) derived by Kiviranta & Kumpulainen (2011).
- 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
$$\operatorname{ssm} = 2a \cdot b \cdot \frac{N_A}{MW} (m^2/g)$$

The derived value from the crystallographic parameters and the molecular mass of montmorillonite is $765 \text{ m}^2/\text{g}$ which is similar to that obtained by Madsen (1998) (749 m²/g).

The interlayer porosity in bentonite depends on the expansion of montmorillonite in contact with 138 139 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 ($h_{\rm IL}$) and 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, 142 Tournassat & Appelo (2011) derived the relation for Na-montmorillonite for the transition of 3 layer 143 144 hydrate to two layer hydrate, following Bourg et al. (2006) and using XRD data from Kozaki et al. (1998, 145 2008):

146
$$h_{II} = x_2 h_{II}^{2WL} + x_3 h_{II}^{3WL}$$

where x_2 and x_3 are the fractions of 2 layer hydrate and 3 layer hydrate, respectively with x2+x3=1. The parameters h_{1L}^{2WL} (0.62 nm) and h_{1L}^{3WL} (0.94 nm) are the thicknesses of these hydrate layers. The fraction x_2 varies between the montmorillonite dry density 1.3 kg/dm³ (minimum) and 1.6 kg/dm³ (maximum) according to:

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

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

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

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

where f_d is the density ratio of water in the interlayer and in the external pores and w_{mm} is the mass 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
- 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
- density the effect of ionic strength on interlayer porosity is small (within 1%).
- 168 <u>Diffuse double layer (DDL) and " free" water porosities:</u>

(3)

(2)

- 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

(6)

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

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

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

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

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

190 The remaining porosity of the "free" solution is:

191
$$\varepsilon_{\text{free}} = \varepsilon_{\text{tot}} - \varepsilon_{\text{IL}} - \varepsilon_{\text{DDL}}$$
(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 the fraction of ε_{DDL} under different assumptions regarding n_c and f_{DLL} . The dependence of IL and DDL 195 porosities as function of ionic strength for a bentonite dry density of 1.56 kg/dm³ and w_{mm} = 0.75 is 196 197 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

- by BET measurements (Bradbury & Baeyens 2002) indicating an external surface area of ~30 m²/g. This
- 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 a. 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

Fig. 2: Distribution of interlayer (IL) and diffuse double layer (DDL) porosity as function of ionic
strength for different stacking numbers (n_c) and corresponding external surfaces areas (A_{ext}).
Left: stacking number of 5. Right: stacking number of 25. Blue lines: sum of IL and DDL porosity
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

porosity distribution, which cannot be directly assessed, namely the stacking number n_c and the number
 of Debye lengths f_{DDL}. As discussed in Tournassat & Appelo (2011), diffusion data (see below) may help

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
- 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
- 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 kg/dm³)
- 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
- porosity and the external solution. An important parameter in their model was the external surface area
 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
- number of 4.8, a Debye length multiplier of 5.0 and an internal surface area of 487 m^2/g were
- 244 estimated.
- A systematic evaluation of anion-accessible porosity data (Muurinen et al. 1989; 2004; 2007; Molera et
- al. 2003; Van Loon et al. 2007) was done by Tournassat & Appelo (2011). The large scatter in the data
- was highlighted, likely explained by different composition and preparation of samples as well as the
 measurement procedure. Nevertheless, fairly good agreement between experimental and modelled
- measurement procedure. Nevertheless, fairly good agreement between experimental and modelled
 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
- water layer at high densities. The authors explained their model result by changes in the microstructure
- 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
- assumed stacking number of 1. The negatively charged surface is compensated by a surplus of cations in
- this space according to the Donnan approximation in which the surface potentials and ion
- 260 concentrations in the DDL are averaged according to:

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

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

267
$$\sum_{i} z_{i} c_{D,i} + q = 0 \text{ (mol/L)}$$
 (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

- external DDL) is the fewer number of structural parameters required. For example, the porosity fraction
- 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
- 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
- AFI models the interlayer surface charge is completely screened by exchangeable cations, whereas this
- is not the case in DS models. In fact, in most simple DS model no screening of the negative surface
- charge is assumed, and cations are distributed between the free solution and the DDL according
 Donnan equilibrium. Thus, the concentrations of cations in the Donnan space are governed by charge,
- but not by chemical constraints. The selectivity of exchangeable cations, can however be considered by
- partial screening of the surface with surface complexed (immobile) cations (Appelo & Wersin 2007;
- 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
- best of our knowledge- not been assessed in a systematic way. However, a few very recent modelling
- studies have been carried out on experimental diffusion data. Tournassat & Steefel (2015) presented
- two DS modelling exercises for simulating the experimental data of Tachi & Yotsuji (2014) and of Glaus et al. (2013). In both cases partial screening of the surface charge by cations sorbed in the Stern layer
- was assumed. The simulated breakthrough behaviour of the anionic (l[°]) and other tracers (HTO, ²²Na⁺,
- $^{137}Cs^+$) showed a good match with the experimental data of Tachi & Yotsuji (2014) which involved ionic
- strength of 0.1 M NaClO₄. In the case of the second dataset of Glaus et al. (2013) diffusion of 22 Na⁺
- 291 under salinity gradient in two diffusion experiments was modelled. An equally good match of the
- 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
- 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
- 8 Appelo 2013) and CrunchFlowMC (Steefel et al. 2014), which are so far the only reactive transport
- 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
- 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
- compensated in the DDL by the cation-enriched solution.

- Both cases build on the well-established thermodynamic bentonite models (Wieland et al. 1994; Wersin
- 2003; Bradbury & Baeyens 2003) developed on the basis of experimental data at low compaction
- 318 (Wanner et al. 1992; Bradbury & Baeyens 1997; 2002; Muurinen & Lehikoinen 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).
- However, the dissolution/precipitation of selected accessory minerals, such as gypsum, calcite, quartz
- and kaolinite is included in the model.

324 <u>AFI model:</u>

- 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
- 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
- al. (2009) and moreover such a number leads to fairly high proportion of IL (eq. 4) as opposed to the DS
- 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
- Borkovec & Westall (1983) is applied which is implemented in PHREEQC and has been used in previous
- studies (Curti & Wersin 2002; Wersin 2003; Wersin et al. 2004). The parameters for cation exchange and
- surface complexation were also selected from those studies and are listed in Table 1.

337 <u>DS model:</u>

- As outlined above, the IL and DDL are considered as a single Donnan space. The distribution of cations
- 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.
- Scoping calculations revealed that, owing to the high surface charge, the Donnan space becomes large
 at lower ionic strength. Application of eq. (7) at high densities points to Debye lengths smaller than one,
 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

353 354

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

	Unit	AFI model	DS model	Comment
Structural parameters				
Specific montmorillon. surface area	m²/g	765	765	see text
TOT stacking number	_	15	1	п
DDL length multiplier		1	<1,variable	see text
Montmorillonite mass fraction		0.75	0.75	н
DDL parameters				
Model used for diffuse layer		DDL*	Donnan	DDL*: Borkovec & Westall 1983
Considered porosity		external	int.+ext.	
Cation avelance neromators				
Cation exchange parameters	og /kg	0 797	0 797	Bradhury & Baoyons 2002
	ец/кg	0.787 Na 0.878	0.787	Bradbury & Baeyens 2002
	eauiv.	Ca 0.084	2	
Initial occupancies	fraction	Mg 0.051		Bradbury & Baeyens 2002
		K 0.017		
				Gaines-Thomas convention used
logK _{Na/Ca}		0.41		for cation exchange model
logK _{Na/Mg}		0.31		н
logK _{Na/K}		0.60		п
Surface complexation parameters				
Surface site concentration	eq/kg	0.0284	0.0284	Wieland et al. 1994
Surface area	m²/g	31.5	31.5	Bradbury & Baeyens 2002
$logK: \equiv SOH + H^+ = \equiv SOH_2^+$		5.4	5.4	Wieland et al. 1994
$\log K: \equiv SOH = \equiv SO^{-} + H^{+}$		-6.7	-6.7	п
Dissolution of accessories / inventor	ies			
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
$CaSO_4 \cdot 2H_2O \leftrightarrow Ca^{2+} + SO_4^{2-} + 2H_2O$	logK	-4.61	-4.61	Giffaut et al. 2014
Calcite ¹	wt%	0.7	0.7	Madsen 1998
$CaCO_3 \leftrightarrow Ca^{2+} + CO_3^{2-}$	logK	-8.48	-8.48	Giffaut et al. 2014
Quartz	wt%	10-15	10-15	Madsen 1998
$SiO_2 + 2H_2O \leftrightarrow H_4SiO_4$	logK	-3.74	-3.74	Giffaut et al. 2014
Kaolinite ¹	wt%	Traces	Traces	Madsen 1998
$AI_2SI_2O_5(OH)_4 + 6H^{+} \leftrightarrow 2AI^{+3} +$	1	C F 1	C = 4	
$H_4SiO_4 + H_2O$	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

- at about 400 m depth below surface. The deposition holes and the overlying deposition tunnel aresurrounded by variably fractured gneissic host rock.
- 363 The target density of the buffer is 2.0 kg/dm³ at full saturation, thus corresponding to a dry density of
- 364 1.57 kg/dm³. 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
- the one hand by the rate of water inflow and on the other by coupled thermo-hydro-mechanical
- behaviour in the buffer which is affected by elevated temperatures in the contacting canister (Posiva
- 2013a). Thus, saturation times will vary and have been estimated to be in the range of decades to
 several hundreds of years (Posiva 2013a). Upon saturation, hydromechanical conditions will become
- several hundreds of years (Posiva 2013a). Upon saturation, hydromechanical conditions will become
 more stable, due to the low hydraulic conductivity (~10⁻¹³-10⁻¹⁴ m/s) and high swelling pressure (6–8
- 373 MPa) (Karnland et al. 2006) and slow diffusive transport will dominate.





- 375Fig. 3:Schematic view of KBS-3 repository components (Posiva 2012). Of interest here are the376bentonite buffer blocks surrounding the canister.
- 377

The groundwater composition at repository depth is fairly saline, Na-Cl dominated with a ionic strength of ~0.2 M and total dissolved solids (TDS) of ~10g/L (Table 2). Due to continuing land uplift and climatic changes, the groundwater at repository level is predicted to become more dilute and more influenced by shallower brackish groundwaters with time (Posiva 2013a). Depending on the conditions, it has been 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

- defined (Hellä et al. 2014). These serve to bound the range of groundwater composition in contact with the bentonite buffer. For that purpose, specific groundwater compositions based on samples from deep
- 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
- 2002). Here we assume that in the beginning of the analysis the buffer is fully saturated and that the
- thermal pulse arising from the decay of short lived nuclides in the waste has dissipated. We consider
 diffusive equilibration between bentonite porewater and the surrounding groundwater, but also a case
- 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).

	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
lonic strength	215.1	243.2	242.5	454.1	18.9	91.9	94.8	95.5
рН	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
К	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
Са	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
CO₃(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

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).

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)
- 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
- 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
- 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

423Table 3: Model scenarios for deriving porewater composition of bentonite buffer. Fractions of424different porosity types (IL: interlayer; DDL: diffuse double layer, "free") also shown (see425text)

Model	Model	Contacting	Assumption	% IL	%DDL	%"free"
scenario	approacn	groundwater	for chioride			
AFI_saline_a	AFI	Saline type	$[CI]_{free} = [CI]_{gw}$	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	$[CI]_{free} = [CI]_{gw}$	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	$[CI]_{free} = [CI]_{gw}$	0	78.8	31.2
DS_dilute	DS	Dilute type	[CI] _{free} = [CI] _{gw}	0	95.7	4.3

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

427 <u>Calculation of porosity distributions:</u>

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 THERMOCHIMIE 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 in439 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
- results, which a priori was not expected in view of the very distinct model assumptions with regard
- 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
- 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
- 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

		Saline case		Dilute case		
Model	DS	AFI	AFI	DS	AFI	AFI
Constraint	diffusive eq.	diffusive eq.	mixing	diffusive eq.	diffusive eq.	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
К	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
Са	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
С	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-0 ⁻	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
КХ		19.6	19.7		72.3	70.7

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473 The concentrations of anions (Cl, SO_4) in the diffuse layer are lower compared to the "free" water

because of the effect of the negative surface charge. They are also affected by the ionic strength,thus decreased in the dilute case.

476 **3.5 Discussion**

477 <u>Application of "reference porewater" concept:</u>

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 example corrosion of the copper canister (Posiva 2013a). They also are used to derive retention 482 483 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 geochemical model and the uncertainties of the derived porewater composition play an important 488 489 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

and proton exchange capacity and the presence of reactive accessory minerals, such as gypsum andcalcite.

496 Larger differences arise when equilibration between the porewater and surrounding groundwater is497 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:

As outlined in section 2.2, multicomponent diffusion through compacted bentonite has been 507 508 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).

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

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 model, the activity coefficients of species in the diffuse layer are commonly assumed to be the same 537 538 as in the "free" porewater (Appelo et al. 2010; Steefel et al. 2014). This assumption is questionable, in particular for cations whose concentrations are in molar range. Activities may be affected by the 539 540 high surface charge (Tournassat & Appelo 2015), ion pair formation (Charlet & Tournassat 2005; Bourg & Sposito 2011) and the decreased dielectric constant of water (Teschke et al. 2001). The 541 activity of divalent cations Ca²⁺ and Mg²⁺ is expected to be more influenced than that of Na⁺ (Ferrage 542

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 10⁵ to 10⁶ 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
- 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
- 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
- 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