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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

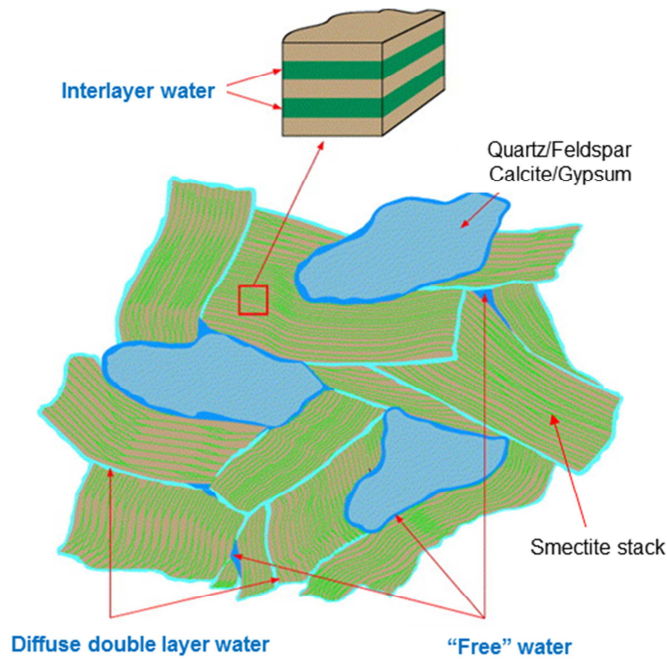
85 & Karnland 2009). Birgersson & Karnland (2009) postulated an osmotic model in which the entire  
86 porespace is considered as Donnan space where both cations and anions reside. More recently, a  
87 double porosity model including DDL and free water has been applied for describing simultaneous  
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.



RIPT

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  $A_{\text{int}}$  ( $\text{m}^2/\text{kg}$ ) 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  $765 \text{ m}^2/\text{g}$  which is similar to that obtained by Madsen (1998) ( $749 \text{ m}^2/\text{g}$ ).

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 ( $\rho_{dry}$ ):  $h_{IL} = 1.41 \cdot 10^{-9} - 4.9 \cdot 10^{-13} \cdot \rho_d$ , 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  $1.3 \text{ kg}/\text{dm}^3$  (minimum) and  $1.6 \text{ kg}/\text{dm}^3$  (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  $\text{kg}/\text{dm}^3$  and  $c$  is the concentration of NaCl in the "free"  
153 external solution.

154 From the internal surface area  $A_{int}$  ( $\text{m}^2/\text{g}$ ) 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  $\text{kg}/\text{dm}^3$ . Considering the buffer target dry density  $1.57 \text{ kg}/\text{dm}^3$  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 ( $A_{\text{ext}}$ ) 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 ( $d_{\text{DDL}}$ ) (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  $f_{\text{DDL}}$  is the number of Debye-lengths. The  $d_{\text{DDL}}$  has  
 186 been shown to be difficult to constrain from experimental data in compact clays and  $f_{\text{DDL}}$  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:

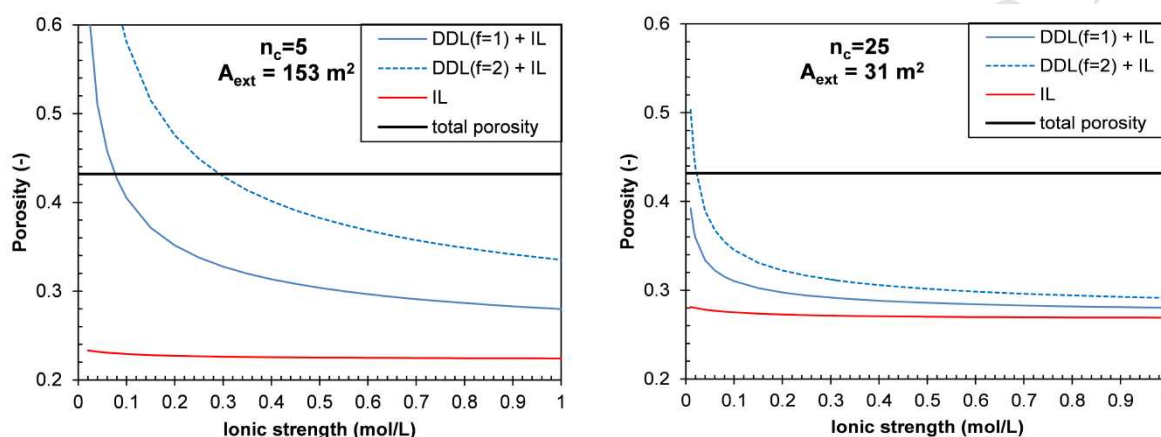
$$189 \quad \varepsilon_{\text{DDL}} = A_{\text{ext}} \cdot d_{\text{DDL}} \cdot w_{\text{mm}} \cdot \rho_d \quad (8)$$

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  $\varepsilon_{\text{DDL}}$  under different assumptions regarding  $n_c$  and  $f_{\text{DDL}}$ . The dependence of IL and DDL  
 196 porosities as function of ionic strength for a bentonite dry density of  $1.56 \text{ kg/dm}^3$  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  $\sim 25$  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  $\sim 15$  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 20m<sup>2</sup>/g for all densities or varied from 15-140 m<sup>2</sup>/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 m<sup>2</sup>/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  $\psi_D$  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.  $\leq 1$  (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<sup>-</sup>) and other tracers (HTO, <sup>22</sup>Na<sup>+</sup>,  
289 <sup>137</sup>Cs<sup>+</sup>) showed a good match with the experimental data of Tachi & Yotsuji (2014) which involved ionic  
290 strength of 0.1 M NaClO<sub>4</sub>. In the case of the second dataset of Glaus et al. (2013) diffusion of <sup>22</sup>Na<sup>+</sup>  
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 m<sup>2</sup>/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   |
|---|-------------------|---|-------------|---|
| <b>Structural parameters</b>  |                   |   |             |   |
| Specific montmorillon. surface area   | m <sup>2</sup> /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        | "   |
| <b>DDL parameters</b>   |                   |   |             |   |
| Model used for diffuse layer  |                   | DDL*  | Donnan      | DDL*: Borkovec & Westall 1983                           |
| Considered porosity   |                   | external                                    | int.+ext.   |   |
| <b>Cation exchange parameters</b>   |                   |   |             |   |
| CEC   | eq/kg             | 0.787                                       | 0.787       | Bradbury & Baeyens 2002                                 |
| Initial occupancies   | equiv. fraction   | Na 0.848<br>Ca 0.084<br>Mg 0.051<br>K 0.017 |             | Bradbury & Baeyens 2002                                 |
| logK <sub>Na/Ca</sub>   |                   | 0.41  |             | Gaines-Thomas convention used for cation exchange model |
| logK <sub>Na/Mg</sub>   |                   | 0.31  |             | "   |
| logK <sub>Na/K</sub>  |                   | 0.60  |             | "   |
| <b>Surface complexation parameters</b>  |                   |   |             |   |
| Surface site concentration  | eq/kg             | 0.0284                                      | 0.0284      | Wieland et al. 1994                                     |
| Surface area  | m <sup>2</sup> /g | 31.5  | 31.5        | Bradbury & Baeyens 2002                                 |
| logK: ≡SOH + H <sup>+</sup> = ≡SOH <sub>2</sub> <sup>+</sup>  |                   | 5.4   | 5.4         | Wieland et al. 1994                                     |
| logK: ≡SOH = ≡SO <sup>-</sup> + H <sup>+</sup>  |                   | -6.7  | -6.7        | "   |
| <b>Dissolution of accessories / inventories</b>   |                   |   |             |   |
| NaCl  | mol/kg            | 1.35E-03                                    | 1.35E-03    | Bradbury & Baeyens 2002, complete dissolution           |
| Gypsum <sup>1</sup>   | mol/kg            | 0.0235                                      | 0.0235      | Bradbury & Baeyens 2002                                 |
| CaSO <sub>4</sub> ·2H <sub>2</sub> O ↔ Ca <sup>2+</sup> + SO <sub>4</sub> <sup>2-</sup> + 2H <sub>2</sub> O   | logK              | -4.61                                       | -4.61       | Giffaut et al. 2014                                     |
| Calcite <sup>1</sup>  | wt%               | 0.7   | 0.7         | Madsen 1998   |
| CaCO <sub>3</sub> ↔ Ca <sup>2+</sup> + CO <sub>3</sub> <sup>2-</sup>  | logK              | -8.48                                       | -8.48       | Giffaut et al. 2014                                     |
| Quartz <sup>1</sup>   | wt%               | 10–15                                       | 10–15       | Madsen 1998   |
| SiO <sub>2</sub> + 2H <sub>2</sub> O ↔ H <sub>4</sub> SiO <sub>4</sub>  | logK              | -3.74                                       | -3.74       | Giffaut et al. 2014                                     |
| Kaolinite <sup>1</sup>  | wt%               | Traces                                      | Traces      | Madsen 1998   |
| Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub> + 6H <sup>+</sup> ↔ 2Al <sup>3+</sup> + H <sub>4</sub> SiO <sub>4</sub> + H <sub>2</sub> O | logK              | 6.51  | 6.51        | Giffaut et al. 2014                                     |

355 <sup>1</sup> excess of these minerals assumed in all calculations

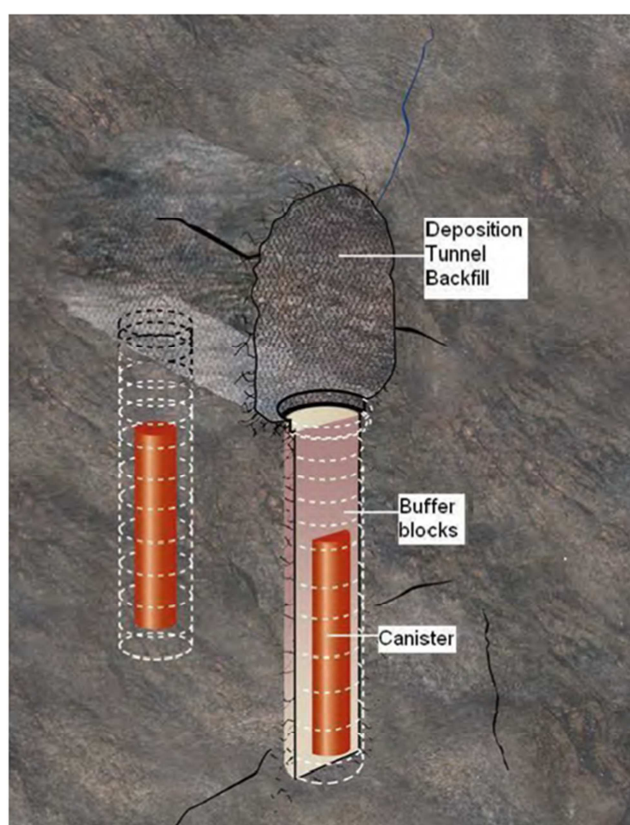
### 356 3. Application to the bentonite buffer at the Olkiluoto site

#### 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  $2.0 \text{ kg/dm}^3$  at full saturation, thus corresponding to a dry density of  
 364  $1.57 \text{ kg/dm}^3$ . 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 ( $\sim 10^{-13}$ – $10^{-14} \text{ m/s}$ ) 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 CO<sub>2</sub> (pCO<sub>2</sub>)  
399 corresponding to atmospheric conditions (10<sup>-3.44</sup> 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 pCO<sub>2</sub>, 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<sub>w</sub> 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<br>Constraint |             | DS<br>diff. eq.  | AFI<br>diff. eq. | AFI<br>mixing |             | DS<br>diff. eq.  | AFI<br>diff. eq. | AFI<br>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 <sup>1</sup>  | 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 <sub>3</sub> (tot)    | 0.66        | 0.64             | 0.66             | 0.53          | 4.50        | 2.56             | 2.58             | 2.56          |
| SO <sub>4</sub>          | 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 <sub>2</sub> )   | -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 <sup>1</sup> [Alk] = [HCO<sub>3</sub><sup>-</sup>]<sub>T</sub> + 2[CO<sub>3</sub><sup>2-</sup>]<sub>T</sub> where subscript T refers to the total concentration of HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>, 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<br>Constraint             | Saline case         |                      |               | Dilute case         |                      |               |
|---------------------------------|---------------------|----------------------|---------------|---------------------|----------------------|---------------|
|                                 | DS<br>diffusive eq. | AFI<br>diffusive eq. | AFI<br>mixing | DS<br>diffusive eq. | AFI<br>diffusive eq. | AFI<br>mixing |
| <b>DDL</b>                      |                     |                      |               |                     |                      |               |
| % 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 <sup>-</sup>               | 72.8                | 692.9                | 662.1         | 61.4                | 113.4                | 115.3         |
| >S-OH <sub>2</sub> <sup>+</sup> | 3.8                 | 28.6                 | 32.5          | 42.8                | 10.7                 | 10.3          |
| <b>Interlayer (IL)</b>          |                     |                      |               |                     |                      |               |
| % total porosity                | 0%                  | 61.0%                | 61.0%         | 0%                  | 63.1%                | 63.1%         |
| NaX                             |                     | 1995.2               | 2100.0        |                     | 1000.2               | 978.8         |
| CaX <sub>2</sub>                |                     | 1257.7               | 1208.2        |                     | 1152.4               | 1125.3        |
| MgX <sub>2</sub>                |                     | 89.3                 | 86.8          |                     | 640.7                | 626.6         |
| KX                              |                     | 19.6                 | 19.7          |                     | 72.3                 | 70.7          |

472

473 The concentrations of anions (Cl, SO<sub>4</sub>) 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).

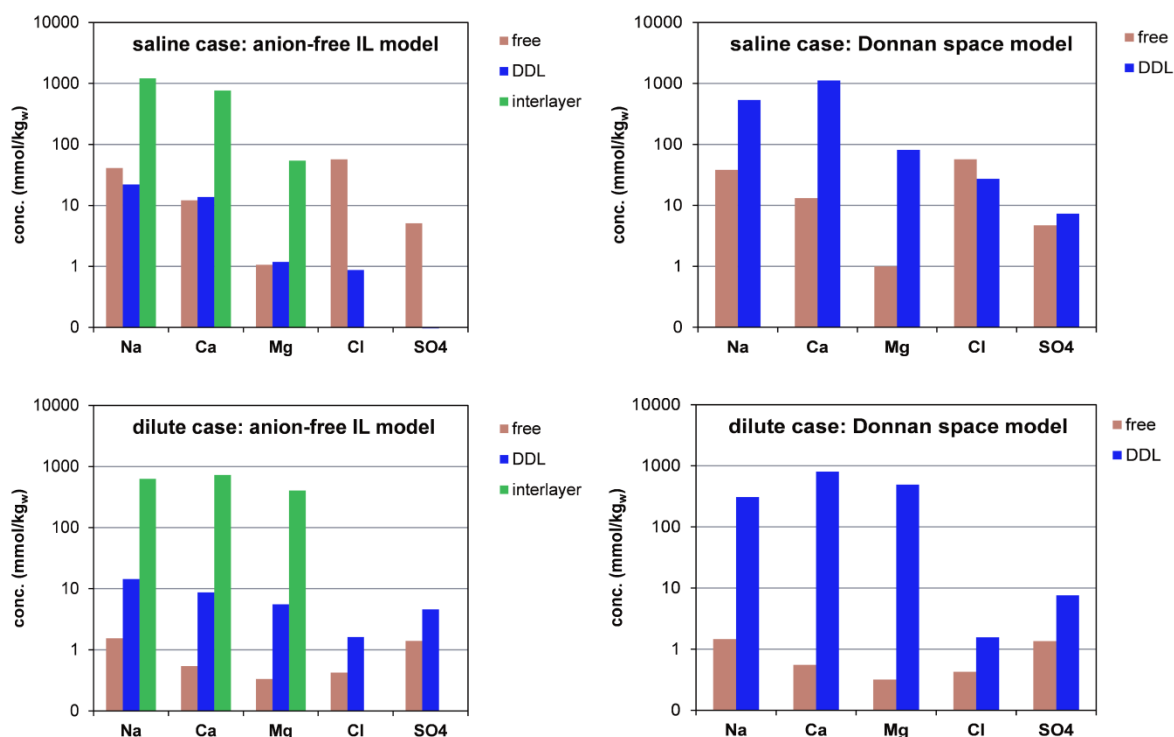
506 Basis for multicomponent diffusion modelling:

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  $\text{Cl}^-$  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  $\text{Cl}^-$  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  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  is expected to be more influenced than that of  $\text{Na}^+$  (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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#### 583 **5. References**

- 584 Alt-Epping, P., Tournassat, C., Rasouli P., Steefel, C.I., Mayer, K.U., Jenni, A., Mäder, U., Sengor, S.S.,  
585 Fernández, R., 2014. Benchmark reactive transport simulations of a column experiment in  
586 compacted bentonite with multispecies diffusion and explicit treatment of electrostatic effects.  
587 *Comput. Geosci.*, DOI 10.1007/s10596-014-9451-x.
- 588 Altmann, S., 2008. ‘Geo’chemical research: A key building block for nuclear waste disposal safety  
589 cases. *J. Contam. Hydrol.* 102, 174-179.
- 590 Andra, 2005. Dossier 2005 Argile: Safety evaluation of a geological repository, Châtenay-Malabry,  
591 France.
- 592 Appelo, C.A.J., 2013. A review of porosity and diffusion in bentonite. Posiva Working Report WR-  
593 2013-29, Posiva Oy, Eurajoki, Finland. [http://www.posiva.fi/en/databank/working\\_reports/](http://www.posiva.fi/en/databank/working_reports/).

- 594 Appelo, C.A.J., Wersin, P., 2007. Multicomponent diffusion modeling in clay systems with application  
595 to the diffusion of tritium, iodide and sodium in Opalinus Clay. *Environ. Sci. Technol.* 41, 5002-  
596 5007.
- 597 Appelo, C.A.J., Van Loon, L.R., Wersin, P., 2010. Multicomponent diffusion of a suite of tracers (HTO,  
598 Cl, Br, I, Na, Sr, Cs) in a single sample of Opalinus Clay. *Geochim. Cosmochim. Acta* 74, 1201-  
599 1219.
- 600 Arcos, D., Grandia, F., Domenech, C., 2006. Geochemical evolution of the near field of a KBS-3  
601 repository. SKB Technical Report TR-06-16, Stockholm Sweden.  
602 <http://www.skb.com/publications/>.
- 603 Baeyens, B., Bradbury, M.H., 1997. A mechanistic description of Ni and Zn sorption on Na-  
604 montmorillonite. Part I: Titration and sorption measurements. *J. Contam. Hydrol.* 27, 199-222.
- 605 Birgersson, M., Karnland, O., 2009. Ion equilibrium between montmorillonite interlayer space and an  
606 external solution —Consequences for diffusional transport. *Geochim. Cosmochim. Acta* 73,  
607 1908-1923.
- 608 Borkovec, M., Westall, J. 1983., Solution of the Poisson-Boltzmann equation for surface excesses of  
609 ions in the diffuse layer at the oxide-electrolyte interface. *J. Electroanal. Chem.* 150, 325-337.
- 610 Bourg, I.C., Sposito, G., 2011. Molecular dynamics simulations of the electrical double layer on  
611 smectite surfaces contacting concentrated mixed electrolyte (NaCl–CaCl<sub>2</sub>) solutions. *J. Colloid*  
612 *Interf. Sci.* 360, 701-715.
- 613 Bourg, I.C., Sposito, G., Bourg, A.C.M., 2006. Tracer diffusion in compacted, water-saturated  
614 bentonite. *Clays Clay Min.* 54, 363-374.
- 615 Bradbury, M.H., Baeyens, B., 1997. A mechanistic description of Ni and Zn sorption on Na-  
616 montmorillonite. Part II. Modelling. *J. Contam. Hydrol.* 27, 223-248.
- 617 Bradbury, M.H., Baeyens, B., 2002. Porewater chemistry in compacted re-saturated MX-80  
618 bentonite: physico-chemical characterisation and geochemical modelling. Nagra Technical  
619 Report NTB 01-08, Wettingen, Switzerland.  
620 [http://www.nagra.ch/en/cat/publikationen/technicalreports-ntbs/ntbs-2001-](http://www.nagra.ch/en/cat/publikationen/technicalreports-ntbs/ntbs-2001-2013/downloadcentre.htm)  
621 [2013/downloadcentre.htm](http://www.nagra.ch/en/cat/publikationen/technicalreports-ntbs/ntbs-2001-2013/downloadcentre.htm).
- 622 Bradbury, M.H., Baeyens, B., 2003. Porewater chemistry in compacted re-saturated MX-80  
623 bentonite. *J. Contam. Hydrol.* 61, 329-338.
- 624 Bradbury, M.H., Berner, U., Curti, E., Hummel, W., Kosakowski, G., Thoenen, T., 2014. Evolution of  
625 the near-field of a HLW repository. Nagra Technical Report NTB 12-01, Wettingen, Switzerland.  
626 [http://www.nagra.ch/en/cat/publikationen/technicalreports-ntbs/ntbs-2001-](http://www.nagra.ch/en/cat/publikationen/technicalreports-ntbs/ntbs-2001-2013/downloadcentre.htm)  
627 [2013/downloadcentre.htm](http://www.nagra.ch/en/cat/publikationen/technicalreports-ntbs/ntbs-2001-2013/downloadcentre.htm).
- 628 Bruno, J., Arcos, D., Duro, L., 1999. Processes and features affecting the near field hydrochemistry.  
629 Groundwater - bentonite interactions. SKB Technical Report TR-99-29, Stockholm, Sweden.  
630 <http://www.skb.com/publications/>.
- 631 Charlet, L., Tournassat, C., 2005. Fe(II)-Na(I)-Ca(II) cation exchange on montmorillonite in chloride  
632 medium : evidence for preferential clay adsorption of ions pairs in marine environment  
633 chemical modelling and XRD profile modelling study. *Aquat. Geochem.* 11, 115-137.
- 634 Cuevas, J., Villar, M.V., Fernández, P., Gómez, P., Martín, P.L., 1997. Pore waters extracted from  
635 compacted bentonite subjected to simultaneous heating and hydration. *Appl. Geochem.* 12,  
636 473-481.
- 637 Curti, E., Wersin, P., 2002. Assessment of porewater chemistry in the bentonite backfill for the Swiss  
638 SF/HLW repository. Nagra Technical Report NTB 02-09, Wettingen, Switzerland.

- 639 <http://www.nagra.ch/en/cat/publikationen/technicalreports-ntbs/ntbs-2001->  
640 [2013/downloadcentre.htm](http://www.nagra.ch/en/cat/publikationen/technicalreports-ntbs/ntbs-2001-2013/downloadcentre.htm).
- 641 Ferrage, E., Tournassat, C., Rinnert, E., Charlet, L., Lanson, B., 2005. Experimental evidence for  
642 calcium-chloride ion pairs in the interlayer of montmorillonite. A XRD profile modeling  
643 approach. *Clays Clay Miner.* 53, 348-360.
- 644 Giffaut, E., Grivé, M., Blanc, P., Vieillard, P., Colàs, E., Gailhanou, H., Gaboreau, S., Marty, N., Madé,  
645 B., Duro, L. 2014. ANDRA thermodynamic database for performance assessment:  
646 *ThermoChimie. Appl. Geochem.* 49, 225–236.
- 647 Glaus, M.A., Frick, S., Rossé, R., Van Loon, L.R., 2010. Comparative study of tracer diffusion of HTO,  
648  $^{22}\text{Na}^+$  and  $^{36}\text{Cl}^-$  in compacted kaolinite, illite and montmorillonite. *Geochim. Cosmochim. Acta*  
649 74, 1999-2010.
- 650 Glaus, M.A., Birgersson, M., Karnland, O., Van Loon, L.R., 2013. Seeming steady-state uphill Diffusion  
651 of  $^{22}\text{Na}^+$  in compacted montmorillonite. *Environ. Sci. & Technol.* 47, 11522-11527.
- 652 Hellä, P., Pitkänen, P., Löfman, J., Partamies, S., Vuorinen, U., Wersin, P., 2014. Safety case for the  
653 disposal of spent nuclear fuel at Olkiluoto. Definition of reference and bounding groundwaters,  
654 buffer and backfill porewaters. Report Posiva 2014-04, Posiva Oy, Eurajoki, Finland.  
655 [http://www.posiva.fi/en/databank/posiva\\_reports/](http://www.posiva.fi/en/databank/posiva_reports/).
- 656 Jenni, A., Mäder, U., Fernández, R., 2014. Multi-component advective-diffusive transport experiment  
657 in MX-80 compacted bentonite: Method and results of 2<sup>nd</sup> phase of experiment and post  
658 mortem analysis. Nagra Arbeitsbericht NAB 14-22, Nagra, Wettingen, Switzerland.
- 659 Juvankoski, M., Ikonen, K., Jalonen, T. 2012. Buffer Production Line 2012. Design, production and  
660 initial state of the buffer. Report POSIVA 2012-17, Posiva Oy, Eurajoki, Finland.  
661 [http://www.posiva.fi/en/databank/posiva\\_reports/](http://www.posiva.fi/en/databank/posiva_reports/).
- 662 Karnland, O., Olsson, S., Nilsson, U., 2006. Mineralogy and sealing properties of various bentonites  
663 and smectite-rich clay materials. SKB Technical Report TR-06-30, Stockholm, Sweden.  
664 <http://www.skb.com/publications/>.
- 665 Keller, L.M., Seiphoori, A., Gasser, P., Falk, L., Holzer, L., Ferrari, A., 2014. The pore structure of  
666 compacted and partly saturated MX-80 bentonite at different dry densities. *Clays Clay Miner.*  
667 62, 357-372.
- 668 Kiviranta, L., Kumpulainen, S., 2011. Quality control and characterization of bentonite materials.  
669 Posiva Working Report 2011-84, Posiva Oy, Eurajoki, Finland.  
670 [http://www.posiva.fi/en/databank/working\\_reports/](http://www.posiva.fi/en/databank/working_reports/).
- 671 Kozaki, T., Saito, N., Fujishima, A., Sato, S., Ohashi, H., 1998. Activation energy for diffusion of  
672 chloride ions in compacted montmorillonite. *J. Contaminant Hydrology* 35, 67-75.
- 673 Kozaki, T., Inada, K., Sato, S., Ohashi, H., 2001. Diffusion mechanism of chloride ions in sodium  
674 montmorillonite. *J. Contam. Hydrol.* 47, 159-170.
- 675 Kozaki, T., Liu, J., Sato, S., 2008. Diffusion mechanism of sodium ions in compacted montmorillonite  
676 under different NaCl concentration. *Phys. Chem. Earth* 33, 957-961.
- 677 Le Forestier, L., Muller, F., Villieras, F., Pelletier, M., 2010. Textural and hydration properties of a  
678 synthetic montmorillonite compared with a natural Na-exchanged clay analogue. *Appl. Clay Sci.*  
679 48, 18–25.
- 680 Leroy, P., Revil, A., Coelho, D., 2006. Diffusion of ionic species in bentonite. *J. Colloid Interf. Sci.* 296,  
681 248-255.
- 682 Madsen, F.T., 1998. Clay mineralogical investigations related to nuclear waste disposal. *Clay Miner.*  
683 33, 109-129.

- 684 Melkior, T., Gaucher, E.B., Brouard, C., Yahiaoui, S., Thoby, D., Clinard, Ch., Ferrage, E., Guyonnet, D.,  
685 Tournassat, C., Coelho, D., 2009. Na<sup>+</sup> and HTO diffusion in compacted bentonite: Effect of  
686 surface chemistry and related texture. *J. Hydrol.* 370, 9-20.
- 687 Molera, M., Eriksen, T., Jansson, M., 2003. Anion diffusion pathways in bentonite clay compacted to  
688 different dry densities. *Appl. Clay Sci.* 23, 69-76.
- 689 Muurinen, A., 2006. Ion concentration caused by an external solution into the porewater of  
690 compacted bentonite. Posiva Working Report 2006-09, Posiva Oy, Eurajoki, Finland.  
691 [http://www.posiva.fi/en/databank/working\\_reports/](http://www.posiva.fi/en/databank/working_reports/).
- 692 Muurinen, A., Lehtonen, J., 1999. Porewater chemistry in compacted bentonite. *Engineer. Geol.* 54,  
693 207-214.
- 694 Muurinen, A., Penttilä-Hilthunen, P., Uusheimo, K., 1987. Diffusion of chloride and uranium in  
695 compacted sodium bentonite. In *Scientific basis for nuclear waste management XII* (eds. W.  
696 Lutze and R. C. Ewing) Mater. Res. Soc. Symp. Proc. Materials Research Society, Pittsburgh, PA.
- 697 Muurinen, A., Karnland, O., Lehtonen, J., 2004. Ion concentration caused by an external solution  
698 into porewater of compacted bentonite. *Phys. Chem. Earth* 29, 119-127.
- 699 Muurinen, A., Karnland, O., Lehtonen, J., 2007. Effect of homogenization on the microstructure and  
700 exclusion of chloride in compacted bentonite. *Phys. Chem. Earth* 32, 485-490.
- 701 Nagra, 2002. Project Opalinus Clay: Safety report. Demonstration of disposal feasibility for spent  
702 fuel, vitrified high-level waste and long-lived intermediate-level waste (Entsorgungsnachweis).  
703 Nagra Technical Report NTB 02-05, Wetingen, Switzerland.  
704 [http://www.nagra.ch/en/cat/publikationen/technicalreports-ntbs/ntbs-2001-](http://www.nagra.ch/en/cat/publikationen/technicalreports-ntbs/ntbs-2001-2013/downloadcentre.htm)  
705 [2013/downloadcentre.htm](http://www.nagra.ch/en/cat/publikationen/technicalreports-ntbs/ntbs-2001-2013/downloadcentre.htm).
- 706 Neretnieks, I., Liu, L., Moreno, L., 2009. Mechanisms and models for bentonite erosion. SKB  
707 Technical Report TR-09-35, Stockholm, Sweden. <http://www.skb.com/publications/>.
- 708 Ochs, M., Lothenbach, B., Shibata, M., Yui, M., 2004. Thermodynamic modeling and sensitivity  
709 analysis of porewater chemistry in compacted bentonite. *Phys. Chem. Earth* 29, 129-136.
- 710 Ohe, T., Tsukamoto, M., 1997. Geochemical properties of bentonite porewater in high-level waste  
711 repository condition. *Nucl. Technol.* 118, 49-57.
- 712 Parkhurst, D.L., Appelo, C.A.J., 2013. Description of input and examples for PHREEQC version 3: a  
713 computer program for speciation, batch-reaction, one-dimensional transport, and inverse  
714 geochemical calculations. No. 6-A43. US Geological Survey.
- 715 Plaschke, M., Schäfer, T., Bundschuh, T., Ngo Manh, T., Knopp, R., Geckeis, H., Kim J.I., 2001. Size  
716 characterization of bentonite colloids by different methods. *Anal. Chem.* 73, 4338-4347.
- 717 Posiva, 2012. Buffer Production Line 2012 - Design, production and initial state of the buffer. Report  
718 Posiva 2012-17, Posiva Oy, Eurajoki, Finland.  
719 [http://www.posiva.fi/en/databank/posiva\\_reports/](http://www.posiva.fi/en/databank/posiva_reports/).
- 720 Posiva, 2013a. Safety case for the disposal of spent nuclear fuel at Olkiluoto. Performance  
721 assessment 2012. Report Posiva 2012-04, Posiva Oy, Eurajoki, Finland.  
722 [http://www.posiva.fi/en/databank/posiva\\_reports/](http://www.posiva.fi/en/databank/posiva_reports/).
- 723 Posiva, 2013b. Safety case for the disposal of spent nuclear fuel at Olkiluoto. Models and data for  
724 the repository system 2012. Report Posiva 2013-01, Posiva Oy, Eurajoki, Finland.  
725 [http://www.posiva.fi/en/databank/posiva\\_reports/](http://www.posiva.fi/en/databank/posiva_reports/).
- 726 Pusch, R., 2001. The microstructure of MX-80 clay with respect to its bulk physical properties under  
727 different environmental conditions. SKB Technical Report TR-01-08, Stockholm, Sweden.  
728 <http://www.skb.com/publications/>.

- 729 Rotenberg, B., Marry, V., Vuilleumier, R., Malikova, N., Simon, C., Turq, P., 2007. Water and ions in  
730 clays: Unraveling the interlayer/micropore exchange using molecular dynamics. *Geochim.*  
731 *Cosmochim. Acta* 71, 5089–5101.
- 732 Sacchi, E., Michelot, J.-L., Pitsch, H., 2000. Porewater extraction from argillaceous rocks for  
733 geochemical characterisation. Nuclear Energy Agency, OECD, Paris.
- 734 Sena, C., Salas, J., Arcos, D., 2010. Thermo-hydro-geochemical modelling of the bentonite buffer. SKB  
735 Technical Report TR-10-65, Stockholm, Sweden. <http://www.skb.com/publications/>.
- 736 SKB, 2010. Radionuclide transport report for the safety assessment SR-Site. SKB Technical Report TR-  
737 10-50, Stockholm, Sweden. <http://www.skb.com/publications/>.
- 738 SKB (2011): Long-term safety for the final repository for spent nuclear fuel at Forsmark. SKB  
739 Technical Report TR-11-01, Stockholm, Sweden.
- 740 Snellman M., Uotila H., Rantanen J. (1987): Laboratory and modelling studies of sodium bentonite  
741 groundwater interaction. *Mat. Res. Soc. Symp. Proc.* 84, 781-790.
- 742 Steefel C.I., Appelo C. A. J., Arora B., Jacques D., Kalbacher T., Kolditz O., Lagneau V., Lichtner P.C.,  
743 Mayer K.U., Meeussen J.C.L., Molins S., Moulton D., Shao H., Simunek J., Spycher N., Yabusaki  
744 S.B., Yeh G.T. (2014): Reactive transport codes for subsurface environmental simulation.  
745 *Comput. Geosci.* DOI 10.1007/s10596-014-9443-x.
- 746 Tachi, Y., Yotsuji, K., 2014. Diffusion and sorption of Cs<sup>+</sup>, Na<sup>+</sup>, I<sup>-</sup> and HTO in compacted sodium  
747 montmorillonite as a function of porewater salinity: Integrated sorption and diffusion model.  
748 *Geochim. Cosmochim. Acta* 132, 75-93.
- 749 Tachi, Y., Yotsuji, K., Suyama, T., Ochs, M., 2014. Integrated sorption and diffusion model for  
750 bentonite. Part 2: porewater chemistry, sorption and diffusion modeling in compacted systems.  
751 *J. Nucl. Sci. Technol.* 51, 1191-1204.
- 752 Teschke, O., Ceotto, G., De Souza, E.F., 2001. Interfacial water dielectric-permittivity-profile  
753 measurements using atomic force microscopy. *Phys. Rev. E* 64, 011605.
- 754 Tournassat, C., Appelo, C.A.J., 2011. Modelling approaches for anion-exclusion in compacted Na-  
755 bentonite. *Geochim. Cosmochim. Acta* 75, 3698-3710.
- 756 Tournassat, C., Steefel, C.I., 2015. Ionic transport in nano-porous clays with consideration of  
757 electrostatic effects. *Rev. Miner. Geochem.* 80, 287-329.
- 758 Tournassat, C., Neaman, A., Villi ras, F., Bosbach, D., Charlet, L., 2003. Nanomorphology of  
759 montmorillonite particles: Estimation of the clay edge sorption site density by low-pressure gas  
760 adsorption and AFM observations. *Am. Miner.* 88, 1989-1995.
- 761 Tournassat, C., Grangeon, S., Leroy, P., Giffaut, E., 2013. Modeling specific pH dependent sorption of  
762 divalent metals on montmorillonite surfaces. A review of pitfalls, recent achievements and  
763 current challenges. *Am. J. Sci.* 313, 395–451.
- 764 Van Loon, L.R., Glaus, M.A., M ller, W., 2007. Anion exclusion effects in compacted bentonites:  
765 Towards a better understanding of anion diffusion. *Appl. Geochem.* 22, 2356-2552.
- 766 Wanner, H., Albinsson, Y., Karnland, O., Wieland, E., Wersin, P., Charlet, L. 1994. The acid/base  
767 chemistry of montmorillonite. *Radiochim. Acta* 66/67, 157-162.
- 768 Wersin, P., 2003. Geochemical modelling of bentonite porewater in high-level waste repositories. *J.*  
769 *Contam. Hydrol.* 61, 405-422.
- 770 Wersin, P., Curti, E., Appelo, C.A.J., 2004. Modelling bentonite-water interactions at high solid/liquid  
771 ratios: swelling and diffuse double layer effects. *Appl. Clay Sci.* 26, 249-257.
- 772 Wersin, P., Kiczka, M., Rosch, D., 2014a. Safety case for a spent nuclear fuel repository at Olkiluoto.  
773 Radionuclide solubility limits and migration parameters for the canister and the buffer. Report

- 774 Posiva 2012-39, Posiva Oy, Eurajoki, Finland.  
775 [http://www.posiva.fi/en/databank/posiva\\_reports/](http://www.posiva.fi/en/databank/posiva_reports/).
- 776 Wersin, P., Pitkänen, P., Alt-Epping, P., Román-Ross, G., Smith, P., Snellman, M., Trincherro, P.,  
777 Molinero, J., Filby, A., Kiczka, M., 2014b. Sulphide fluxes and concentrations in the spent nuclear  
778 fuel repository at Olkiluoto. Report Posiva 2014-01, Posiva Oy, Eurajoki, Finland.  
779 [http://www.posiva.fi/en/databank/posiva\\_reports/](http://www.posiva.fi/en/databank/posiva_reports/).
- 780 Wieland, E., Wanner, H., Albinsson, Y., Wersin, P., Karnland, O., 1994. A surface chemical model of  
781 the bentonite-water interface and its implications for modelling the near field chemistry in a  
782 repository for spent fuel. SKB Technical Report TR 94-26, Stockholm, Sweden.  
783 <http://www.skb.com/publications/>.



**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