

1 **Solving the Nernst-Planck Equation in Heterogeneous Porous Media with Finite**
2 **Volume Methods: Averaging Approaches at Interfaces**
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13 **Key Points:**

- 14 • Solving the Nernst-Planck equation with a finite volume method requires a proper
15 averaging procedure of properties at grid cell interfaces.
- 16 • Averaging rules commonly applied to diffusion properties can lead to numerical
17 instability and result in inaccuracy in reactive transport codes.
- 18 • Correct averaging schemes were derived for the general case.

19

20 **Abstract**

21 Molecular diffusion of dissolved species is a fundamental mass transport process affecting many
22 environmental and technical processes. Whereas diffusive transport of single tracers can be
23 described by Fick's law, a multicomponent approach based on the Nernst-Planck equation is
24 required for charge-coupled transport of ions. The numerical solution of the Nernst-Planck
25 equation requires special attention with regard to properties that are required at interfaces of
26 numerical cells when using a finite difference or finite volume method. Weighted arithmetic and
27 harmonic averages are used in most codes that can solve the Nernst-Planck equation. This way of
28 averaging is correct for diffusion coefficients, but inappropriate for solute concentrations at
29 interfaces. This averaging approach leads to charge balance problems and thus to numerical
30 instabilities near interfaces separating grid volumes with contrasting properties. We argue that a
31 logarithmic-differential average should be used. Here this result is generalized, and it is
32 demonstrated that it generally leads to improved numerical stability and accuracy of
33 concentrations computed near material interfaces. It is particularly relevant when modeling semi-
34 permeable clay membranes or membranes used in water treatment processes.

35 **1 Introduction**

36 Diffusion of aqueous species in geological or engineered media is a fundamental mass transport
37 process. It is especially important for low permeability geological materials containing
38 significant amount of clay minerals such as clayey shales, engineered materials such as clay
39 barriers, or concrete structures. Their low permeability and diffusion properties make them ideal
40 for waste confinement applications, or technological materials such as filtration membranes used
41 for water treatment. The characterization of diffusion processes is also essential for our ability to
42 understand various hydro-geochemical observations such as isotopic fractionation coupled to
43 transport processes (La Bolle & Fogg, 2001; Peeters et al., 2002; Bourg & Sposito, 2007; La
44 Bolle et al., 2008; Bourg et al., 2010; Rolle et al., 2010), the dynamics of gas-water exchanges
45 (Haghighi et al., 2013; Tokunaga et al., 2017), or the dynamics of contaminant accumulation and
46 release in and from rocks and sediments having very heterogeneous pore structures (Chapman &
47 Parker, 2005; Liu et al., 2006, 2011; Gouze et al., 2008; Robinet et al., 2012; Hadley & Newell,
48 2014; Zachara et al., 2016; Bone et al., 2017). Ultimately, diffusion is the fundamental process
49 that generates mixing of dissolved species, and enables reactive fronts to appear between
50 aqueous solutions having contrasted chemical compositions (Anna et al., 2011, 2013; Le Borgne
51 et al., 2011, 2013).

52 Diffusion processes are the result of random motion of dissolved species subject to thermal
53 agitation, and for which no interactions between the dissolved species are considered. Diffusion
54 processes are commonly simulated with Fick's laws. However, ions are charged species, and
55 their individual diffusion coefficients in solution are dependent on their charge, mass and radius.
56 As a consequence of the electro-neutrality condition in aqueous environments, ions are affected
57 by electrochemical migration effects, and multicomponent diffusion processes are thus better
58 represented by the more general Nernst-Planck formulation rather than by the limiting Fick's
59 laws. The importance of electrostatic interactions among charged species in the modeling of
60 multicomponent diffusion processes was early emphasized to explain vertical profiles of ion
61 concentrations in the pore water of marine sediments, i.e. systems in which diffusion is the
62 dominant transport process (Ben-Yaakov, 1972; Lasaga, 1979; Felmy & Weare, 1991a; b;
63 Giambalvo et al., 2002; Boudreau et al., 2004). Later the importance of multicomponent

64 diffusion in our understanding of mixing processes in porous media has been demonstrated even
 65 for systems whose mass transport is dominated by advective flow (Chiogna et al., 2011;
 66 Muniruzzaman et al., 2014; Muniruzzaman & Rolle, 2015, 2016, 2017; Rasouli et al., 2015;
 67 Rolle et al., 2018). In the field of reactive transport modeling, the use of multicomponent
 68 diffusion models is hindered by two factors: the first one is the scarcity of codes that are able to
 69 handle the Nernst-Planck formulation for the resolution of diffusive fluxes (Steeffel et al., 2015);
 70 the second one is the computational cost associated with the use of the Nernst-Planck
 71 formulation rather than Fick's laws. In the last decade, the use of Nernst-Planck equation instead
 72 of Fick's laws has been shown to be essential to understand the apparent anomalous diffusion
 73 behavior of systems in which the diffusion of charged species is affected by the electrostatic
 74 properties of the surfaces present on the solid phases (Tournassat & Steefel, 2015). Most of the
 75 related studies concerned the properties of clay and concrete materials, which are investigated
 76 with regard to their confinement properties for radionuclides or other toxic solutes (Gvirtzman &
 77 Gorelick, 1991; Appelo & Wersin, 2007; Appelo et al., 2008, 2010; Glaus et al., 2013, 2015; Alt-
 78 Epping et al., 2015, 2018; Tournassat & Steefel, 2015, 2019a; b; Bourg & Tournassat, 2015;
 79 Tinnacher et al., 2016; Appelo, 2017; Gimmi & Alt-Epping, 2018). However, the use of reactive
 80 transport models using the Nernst-Planck formulation can be foreseen to be increasingly
 81 important for the modeling of other types of materials and related applications including
 82 microbial electrochemical cells or membrane filtration technologies (Marcus et al., 2010).

83 The numerical solution of the Nernst-Planck equation in a reactive transport model using a finite
 84 difference/volume method is subject to a range of difficulties when applied to spatially
 85 heterogeneous media (Tournassat & Steefel, 2015; Gimmi & Alt-Epping, 2018). In this study,
 86 we address the problem of the definition of averaged properties at the interface between porous
 87 domains having contrasting properties. This work should facilitate a rigorous implementation of
 88 the Nernst-Planck equation in reactive transport codes.

89 2 Governing equations

90 In absence of an external electric potential, the electrochemical potential μ_i (in $\text{J}\cdot\text{mol}^{-1}$) of an ion
 91 i can be expressed as

$$\mu_i = \mu_i^\circ + RT \ln a_i + z_i F \psi = \mu_i^\circ + RT \ln \frac{\gamma_i m_i}{m^\circ} + z_i F \psi \quad (1)$$

92 where T is the temperature (in K), R is the gas constant ($8.314 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$), F is the Faraday
 93 constant ($96485 \text{ J}\cdot\text{V}^{-1}\cdot\text{mol}^{-1}$), ψ an (internal) electrical potential (V), m° is the standard state
 94 molality ($1 \text{ mol}\cdot\text{kg}^{-1}$), μ_i° is the standard (electro)chemical potential of species i (in $\text{J}\cdot\text{mol}^{-1}$), a_i
 95 is its chemical activity, z_i is its charge number (dimensionless), m_i is its molality (in $\text{mol}\cdot\text{kg}^{-1}$)
 96 and γ_i is its activity coefficient (dimensionless). The diffusive flux $J_{i,s}$ (in $\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$) of an ion
 97 in a solution is given by the Nernst-Planck equation:

$$J_{i,s} = -u_i c_i \nabla \mu_i = -u_i c_i RT \nabla \ln \left(\gamma_i \frac{m_i}{m^\circ} \right) - u_i z_i F c_i \nabla \psi \quad (2)$$

98 where u_i is the mobility of species i (in $\text{mol}\cdot\text{m}^2\cdot\text{s}^{-1}\cdot\text{J}^{-1}$), and c_i is its molarity (in $\text{mol}\cdot\text{m}^{-3}$), which
 99 can be expanded as:

$$c_i = m_i \rho_{solv} \quad (3)$$

100 where ρ_{solv} is the density of the solvent (in $\text{kg}_{\text{solvent}} \cdot \text{m}^{-3}_{\text{solution}}$). The mobility u_i refers here to the
 101 average velocity of a species in solution acted upon by a unit force, independent of the origin of
 102 the force (Steefel & Maher, 2009). The diffusion coefficient D_i (in $\text{m}^2 \cdot \text{s}^{-1}$) of the species i is
 103 proportional to its mobility according to the Nernst-Einstein equation:

$$D_i = RTu_i \quad (4)$$

104 In a porous medium, the diffusion coefficient of the species i is usually described as a function of
 105 the porosity ϕ , of the tortuosity factor τ_i of the medium, which can be specific to each species,
 106 and of the self-diffusion coefficient of the species in solution $D_{i,s}$ (Shackelford, 1991):

$$D_{i,e} = \phi \tau_i D_{i,s} \quad (5)$$

107 The diffusive flux in a porous medium, $J_{i,p}$, can thus be written:

$$J_{i,p} = -D_{i,e} \rho_{solv} m_i \nabla \ln(m_i \gamma_i) - \frac{z_i F D_{i,e} \rho_{solv} m_i}{RT} \nabla \psi \quad (6)$$

108 In one dimension, for the sake of simplicity, Eq. (6) becomes:

$$J_{i,p}^x = -D_{i,e} \rho_{solv} m_i \frac{\partial \ln(m_i \gamma_i)}{\partial x} - \frac{z_i F D_{i,e} \rho_{solv} m_i}{RT} \frac{\partial \psi}{\partial x} \quad (7)$$

109 As an additional simplifying condition, the value of the solvent density is often considered
 110 constant and equal to $1000 \text{ kg}_{\text{solvent}} \cdot \text{m}^{-3}_{\text{solution}}$. It follows:

$$J_{i,p}^x = -D_{i,e} c_i \frac{\partial \ln(c_i \gamma_i)}{\partial x} - \frac{z_i F D_{i,e} c_i}{RT} \frac{\partial \psi}{\partial x} \quad (8)$$

111 In the absence of an external electric field, there is no electrical current and so:

$$\sum_j z_j J_{j,p}^x = 0 \quad (9)$$

112 The combination of equations (7) and (9) provides an expression for the gradient of the diffusion
 113 potential:

$$\frac{\partial \psi}{\partial x} = -\frac{RT}{F} \frac{\sum_j z_j D_{j,e} c_j \frac{\partial \ln(c_j \gamma_j)}{\partial x}}{\sum_j z_j^2 D_{j,e} c_j} \quad (10)$$

114 Consequently, it is possible to express the Nernst-Planck equation with known parameters only,
 115 *i.e.*, concentrations, diffusion coefficients, and activity coefficients:

$$J_{i,p}^x = -D_{i,e} c_i \frac{\partial \ln(c_i \gamma_i)}{\partial x} + z_i D_{i,e} c_i \frac{\sum_j z_j D_{j,e} c_j \frac{\partial \ln(c_j \gamma_j)}{\partial x}}{\sum_j z_j^2 D_{j,e} c_j} \quad (11)$$

116 The Nernst-Planck equation for the diffusion of individual charged species in a porous medium
 117 contains thus two main contributions:

- 118 • a contribution related to the gradient of activity, $-D_{i,e}c_i \frac{\partial \ln(c_i \gamma_i)}{\partial x}$,
 - 119 • and a contribution related to the diffusion potential $+z_i D_{i,e} c_i \frac{\sum_j z_j D_{j,e} c_j \frac{\partial \ln(c_j \gamma_j)}{\partial x}}{\sum_j z_j^2 D_{j,e} c_j}$,
- 120 which arises from the different mobilities of the diffusing species and the zero electrical
 121 current condition.

122 The contribution related to the gradient of activity can be itself split in two contributions:

- 123 • a contribution related to the gradient of concentration $-D_{i,e} \frac{\partial c_i}{\partial x}$, that corresponds to the
 124 Fickian diffusion contribution;
- 125 • and a contribution related to the gradient of activity coefficient $-D_{i,e} c_i \frac{\partial \ln \gamma_i}{\partial x}$.

126 If the diffusive transport processes take place in the presence of a spatially homogeneous
 127 background electrolyte composition the contribution of the activity coefficient gradient can be
 128 omitted and Eq. (11) is simplified to:

$$J_{i,p}^x = -D_{i,e} \frac{\partial c_i}{\partial x} + z_i c_i D_{i,e} \frac{\sum_j z_j D_{j,e} \frac{\partial c_j}{\partial x}}{\sum_j z_j^2 D_{j,e} c_j} \quad (12)$$

129
 130 In addition, if all species have the same diffusion coefficient D_e , Eq. (12) is simplified into:

$$J_{i,p}^x = -D_e \frac{\partial c_i}{\partial x} + z_i c_i D_e \frac{\sum_j z_j \frac{\partial c_j}{\partial x}}{\sum_j z_j^2 c_j} \quad (13)$$

131 Because of the electro-neutrality condition in solution $\sum_j z_j \frac{\partial c_j}{\partial x}$ is equal to zero, and Eq. (13)
 132 reduces then to the Fickian diffusion equation:

$$J_{i,p}^x = -D_e \frac{\partial c_i}{\partial x} \quad (14)$$

133

134 **3 Problem**

135 In the finite difference/volume numerical resolution scheme that is common to most of the
 136 reactive transport codes (Steeffel et al., 2015), the properties of the media, i.e. porosity, tortuosity,

137 and local concentrations, are defined at the center for each grid cell and apply to the whole of
 138 each grid cell. The flux terms, in contrast, have to be evaluated at the interface between two
 139 cells. The activity or concentration gradients between two adjacent cells can be evaluated
 140 directly for this purpose. However, Eqs. (11), (12) and (14) contain several terms that must be
 141 averaged over two adjacent cells. After discretization, with consideration of activity gradients
 142 Eq. (11) becomes:

$$J_{i,p}^x = -\overline{D_{i,e}c_i} \frac{\Delta \ln(c_i \gamma_i)}{\Delta x} + z_i \overline{D_{i,e}c_i} \frac{\sum_j z_j \overline{D_{j,e}c_j} \frac{\Delta \ln(c_j \gamma_j)}{\Delta x}}{\sum_j z_j^2 \overline{D_{j,e}c_j}} \quad (15)$$

143 For the case where activity coefficient gradients are not considered, Eqs. (12) and (14) become,
 144 respectively:

$$J_{i,p}^x = -\overline{D_{i,e}} \frac{\Delta c_i}{\Delta x} + z_i \overline{D_{i,e}c_i} \frac{\sum_j z_j \overline{D_{j,e}} \frac{\Delta c_j}{\Delta x}}{\sum_j z_j^2 \overline{D_{j,e}c_j}} \quad (16)$$

$$J_{i,p}^x = -\overline{D_{i,e}} \frac{\Delta c_i}{\Delta x} \quad (17)$$

145 where \overline{X} represent an average value of the parameter X at the interface between two grid cells.
 146 Reminding that \overline{ABC} , the average of $A \times B \times C$, is not equal to $\overline{A} \times \overline{B} \times \overline{C}$, the product of the
 147 average values, in general, the discretization method on a grid makes it necessary to define
 148 proper averaging methods for the mean values present in Eqs. (15), (16) and (17).

149 Most reactive transport codes handle only Fickian diffusion (Eq. (17)), but some can handle the
 150 Nernst-Planck equation which includes the diffusion potential term (Eqs. (15) and (16); e.g.
 151 Flotran, Crunchflow, MIN3P, and PHREEQC) (Steeffel et al., 2015). Among them, only
 152 PHREEQC resolves the dependence of the flux to the activity coefficient gradient (Appelo &
 153 Wersin, 2007; Appelo et al., 2010; Appelo, 2017). In the Fickian approximation, it is only
 154 necessary to define a proper evaluation of $\overline{D_e}$. Otherwise it is necessary to define the averaging
 155 method for $\overline{D_{i,e}c_i}$ and $\overline{D_{i,e}}$. In the following, rigorous averaging methods are derived for all of
 156 these terms, and the influence of the averaging methods on the computed diffusive flux is
 157 investigated.

158 **4 Mean diffusion transport parameters in two adjacent grid cells**

159 4.1 Fickian approximation and average value of $\overline{D_e}$ at interface

160 In the case where the Fick's diffusion equation applies, the flux $J_{i,p,1 \rightarrow 2}^x$ from grid cell 1 to grid
 161 cell 2 can be written:

$$J_{i,p,1 \rightarrow 2}^x = -\overline{D_e} \frac{c_{i,2} - c_{i,1}}{\frac{\Delta x_2}{2} + \frac{\Delta x_1}{2}} \quad (18)$$

162 where subscripts 1 and 2 indicate that the values are referred to cell 1 and cell 2 respectively. Δx_1
 163 and Δx_2 are the lengths of grid cells 1 and 2 respectively. It is also possible to define $J_{i,p,1 \rightarrow \text{int}}^x$
 164 and $J_{i,p,\text{int} \rightarrow 2}^x$, the flux from the center of cell 1 to the interface and from the interface to the
 165 center of cell 2, where the subscript ‘‘int’’ indicates that the values are referred to the interface
 166 between the two cells. The properties within each cell are homogeneous, and it follows:

$$J_{i,p,1 \rightarrow \text{int}}^x = -D_{e,1} \frac{c_{i,\text{int}} - c_{i,1}}{\frac{\Delta x_1}{2}} \quad (19)$$

$$J_{i,p,\text{int} \rightarrow 2}^x = -D_{e,2} \frac{c_{i,2} - c_{i,\text{int}}}{\frac{\Delta x_2}{2}} \quad (20)$$

167 Under stationary conditions:

$$J_{i,p,1 \rightarrow \text{int}}^x = J_{i,p,\text{int} \rightarrow 2}^x = J_{i,p,1 \rightarrow 2}^x \quad (21)$$

168 and thus:

$$c_{i,\text{int}} = \frac{D_{e,2}c_{i,2}\Delta x_1 + D_{e,1}c_{i,1}\Delta x_2}{D_{e,2}\Delta x_1 + D_{e,1}\Delta x_2} \quad (22)$$

169 Eq. (22) can be reinserted in Eq. (21):

$$\overline{D}_e = \frac{D_{e,2}D_{e,1}(\Delta x_2 + \Delta x_1)}{D_{e,2}\Delta x_1 + D_{e,1}\Delta x_2} \quad (23)$$

170 At steady state, the value of the effective diffusion coefficient at the interface $\overline{D}_{i,e}$ is thus the
 171 weighted harmonic mean of $D_{i,e,2}$ and $D_{i,e,1}$.

172 4.2 Average concentration to be used in the Nernst-Planck equation at interface

173 Gimmi and Alt-Epping (2018) explored this problem in the specific case of a Donnan membrane
 174 system in which a reservoir of electro-neutral solution (subscript 1) was considered to be at
 175 equilibrium with another reservoir (subscript 2) that contained fixed charges. The solution in
 176 reservoir 2 was not electroneutral, and its charge compensated the fixed charges. The fixed
 177 charges were simulated using immobile species ($D_e = 0$), and the system was modeled with the
 178 Nernst-Planck equation. The system was considered to be at equilibrium when the diffusion
 179 fluxes were equal to zero for each of the species. Because of the presence of the fixed charges in
 180 the reservoir 2, solute species concentrations were not equal in reservoirs 1 and 2 at equilibrium
 181 (zero flux condition). In these conditions, they were able to show analytically and numerically
 182 that the average concentration at the interface, $c_{i,\text{int}}$, should be calculated for all mobile species
 183 according to:

$$c_{i,\text{int}} = \frac{c_{i,2} - c_{i,1}}{\ln c_{i,2} - \ln c_{i,1}} \quad (24)$$

184 It is possible to generalize this result to any diffusion problem in transient non-equilibrium
 185 conditions. The activity gradient terms in the Nernst-Planck equation can be expanded into:

$$D_{i,e}c_i \frac{\partial \ln(c_i \gamma_i)}{\partial x} = D_{i,e}c_i \frac{\partial \ln c_i}{\partial x} + D_{i,e}c_i \frac{\partial \ln \gamma_i}{\partial x} \quad (25)$$

186 and the concentration gradient term must respect the following mathematical equality:

$$D_{i,e}c_i \frac{\partial \ln c_i}{\partial x} = D_{i,e} \frac{\partial c_i}{\partial x} \quad (26)$$

187 It follows after discretization on a grid:

$$\overline{D_{i,e}c_i} \frac{\Delta \ln c_i}{\Delta x} = \overline{D_{i,e}} \frac{\Delta c_i}{\Delta x} \quad (27)$$

188 and thus, between two cells 1 and 2:

$$\overline{D_{i,e}c_i} = \overline{D_{i,e}} \frac{c_{i,2} - c_{i,1}}{\ln c_{i,2} - \ln c_{i,1}} \quad (28)$$

189 In a medium with spatially homogeneous properties (constant $D_{i,e}$ value), or generally when the
 190 average $\overline{D_e}$ is independent of the concentrations c_i (as is the case for Eq. (23) as long as the local
 191 $D_{i,e}$ are independent of the pore water chemistry), Eq. (28) becomes:

$$\overline{c_i} = \frac{c_{i,2} - c_{i,1}}{\ln c_{i,2} - \ln c_{i,1}} \quad (29)$$

192 Eq. (29) is identical to Eq. (24), but it was obtained for a more general case, *i.e.* without
 193 requiring equilibrium or steady-state conditions, and without the presence of immobile solute
 194 species. One must note that the terms related to the activity coefficient gradient cancel in Eq.
 195 (25), thus the condition of the absence of activity coefficient gradients is not necessary to apply
 196 in Eq. (28) or (29).

197 This result shows that the simplifications made from Eq. (11) to (12) with the equality
 198 $\frac{\partial \ln y}{\partial x} = \frac{1}{y} \frac{\partial y}{\partial x}$ might result in reduced accuracy of the results obtained after spatial discretization
 199 on a grid. In spatially heterogeneous media, and without any assumptions about equilibrium or
 200 steady-state conditions, Eq. (28) can be combined directly with Eq. (15) to yield:

$$J_{i,p}^x = -\overline{D_{i,e}} \left(\frac{\Delta c_i}{\Delta x} + \frac{\Delta c_i}{\Delta \ln c_i} \frac{\Delta \ln \gamma_i}{\Delta x} \right) + z_i \overline{D_{i,e}} \frac{\Delta c_i}{\Delta \ln c_i} \frac{\sum_j z_j \overline{D_{j,e}} \left(\frac{\Delta c_j}{\Delta x} + \frac{\Delta c_j}{\Delta \ln c_j} \frac{\Delta \ln \gamma_j}{\Delta x} \right)}{\sum_j z_j^2 \overline{D_{j,e}} \frac{\Delta c_j}{\Delta \ln c_j}} \quad (30)$$

201

202 Neglecting the activity coefficient gradients:

$$J_{i,p}^x = -\overline{D_{i,e}} \frac{\Delta c_i}{\Delta x} + z_i \overline{D_{i,e}} \frac{\Delta c_i}{\Delta \ln c_i} \frac{\sum_j z_j \overline{D_{j,e}} \frac{\Delta c_j}{\Delta x}}{\sum_j z_j^2 \overline{D_{j,e}} \frac{\Delta c_j}{\Delta \ln c_j}} \quad (31)$$

203 Eq. (31) leaves $\overline{D_{i,e}}$ as the only average parameter that must be evaluated at the interface
 204 between two grid cells in a spatially heterogeneous system. In any case, the value of $\overline{D_{i,e}}$ can be
 205 obtained with Eq. (23), as the $\overline{D_{i,e}}$ values that enter the Nernst-Planck equation have to
 206 represent the species diffusion coefficients without considering any coupling between different
 207 ions, *i.e.*, just for Fickian transport. Accordingly, Eq. (23) can thus be combined to Eq. (31) to
 208 give the general discretized form of the Nernst-Planck equation in a heterogeneous system.

209 **5 Evaluation of alternative averaging methods on the computation of diffusive fluxes**

210 Reactive transport codes use different types of averaging methods to evaluate the diffusion
 211 parameters at interfaces between cells (Tournassat & Steefel, 2019a), and the influence of
 212 averaging schemes that are different from the correct one, which is given by Eq. (31) combined
 213 with Eq. (23), should then be evaluated. Two simple model systems were set-up to illustrate
 214 these differences.

215 The first system was made by two reservoirs separated by a membrane. Na^+ and Cl^-
 216 concentrations were set to $0.1 \text{ mol}\cdot\text{L}^{-1}$ in the left reservoir and in the membrane, while the right
 217 reservoir contained a solution of $1 \text{ mol}\cdot\text{L}^{-1} \text{ Cl}^-$, $2 \text{ mol}\cdot\text{L}^{-1} \text{ Na}^+$, and $1 \text{ mol}\cdot\text{L}^{-1}$ of a large
 218 monovalent anionic molecule for which the membrane was impermeable. To this end, a
 219 tortuosity factor of zero was specifically assigned to this species in the membrane. Consequently,
 220 all species were able to diffuse through the membrane except the large anionic molecule. The
 221 tortuosity factor of the reservoirs and membrane were set otherwise to 1 for all species. Self-
 222 diffusion coefficients (D_0) were set to $1.3 \cdot 10^{-9} \text{ m}^2\cdot\text{s}^{-1}$, $2.1 \cdot 10^{-9} \text{ m}^2\cdot\text{s}^{-1}$, and $10^{-9} \text{ m}^2\cdot\text{s}^{-1}$ for Na^+ , Cl^-
 223 and the large anionic species. The length of the two reservoirs (porosity of 1) was set to 5 mm
 224 and the thickness of the membrane (porosity of 0.1) was set to 200 μm (Figure 1). Each of the
 225 reservoir domains was discretized into 25 grid cells. The second system differed from the first
 226 one by the absence of the membrane between the two reservoirs, by the size of the grid cells in
 227 the left reservoir (100 μm for a total length of 2.5 mm) and by the presence of different tortuosity
 228 factors for the different species in the two reservoirs: 0.5 for all species in the left reservoir, and
 229 1, 0.7 and 0.2 for Na^+ , Cl^- and the large anionic species respectively in the right reservoir (Figure
 230 2). The charge of the large anionic molecule was also set to -2 and its concentration was
 231 decreased to $0.5 \text{ mol}\cdot\text{L}^{-1}$. Three different averaging methods were tested: the reference method
 232 given by Eq. (31) combined with Eq. (23), and two alternative methods described in Table 1. The
 233 alternative method 1 lumped together the effective diffusion coefficient and the concentration
 234 before harmonic averaging at the interface, while the alternative method 2 computed the
 235 harmonic average of $D_{i,e}$ and multiplied it with the weighted arithmetic average concentration at
 236 the interface. The diffusion calculations were run using the code 3Diff with an explicit, forward
 237 in time and central in space, numerical resolution scheme. This code and its resolution scheme
 238 have been benchmarked successfully with CrunchClay and PHREEQC using the arithmetic
 239 average method (alternative method 2) (Tournassat & Steefel, 2019a).

240 The system 1 is representative of a semi-permeable membrane system for which a Donnan
 241 equilibrium is expected after equilibration. Indeed, the reference model predicted the correct
 242 concentrations in the right reservoir corresponding to the Donnan equilibrium (Figure 1, left), a
 243 result that was consistent with previous findings of Gimmi and Alt-Epping (2018), who showed
 244 the importance of using a logarithmic average for the computation of the concentration at the
 245 interface between two cells when solving the Nernst-Planck equation in the presence of
 246 immobile species. The alternative method 2 also made it possible to predict the correct
 247 concentration, but only far from the membrane-reservoir interfaces. Next to this interface, charge
 248 balance problems occurred, and electroneutrality was not achieved on both sides of the
 249 membrane. This problem illustrates the need to compute correctly the average concentrations in
 250 the interfacial terms of the Nernst-Planck equation. The alternative method 1 resulted in large
 251 deviations from electroneutrality, which ultimately led to large concentration oscillations in the
 252 numerical solution of the transport equation (Figure 1, right). In system 2, which is very
 253 heterogeneous, the reference and the alternative method 2 led to similar results, while the
 254 alternative method 1 resulted in large concentration oscillations after ~ 300 s of simulated time
 255 (Figure 2). The alternative method 2 (arithmetic averaging) is the method commonly used in
 256 reactive transport modeling codes. Our simple intercomparison exercise pointed out the
 257 adequacy of the arithmetic averaging method for problems, in which membrane behavior and
 258 large electrolyte concentration gradients are not present.

259

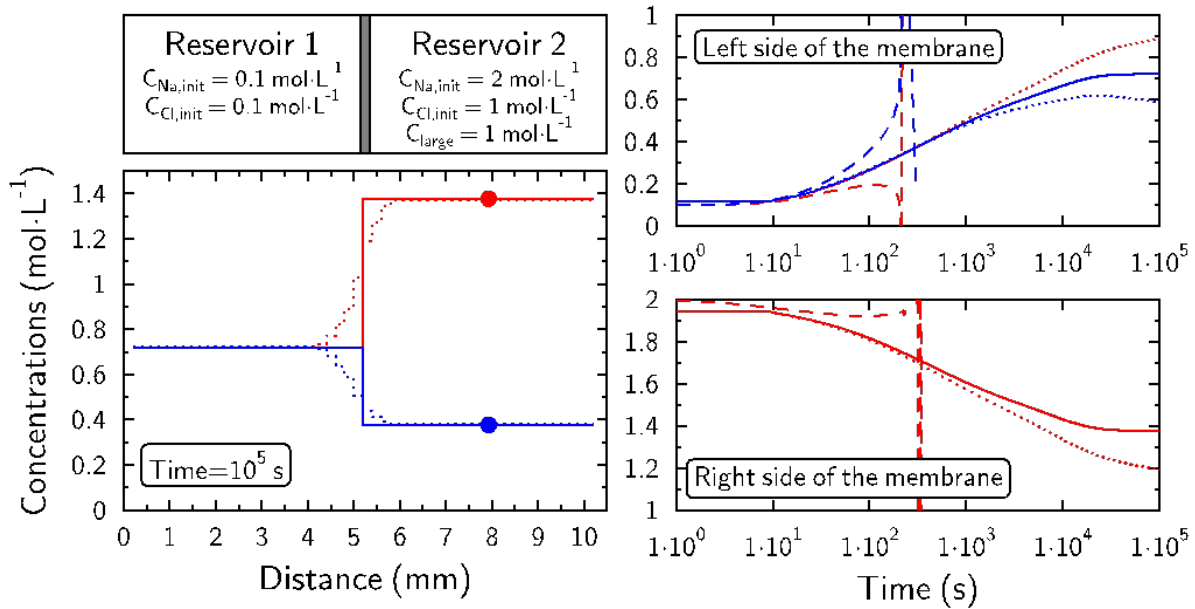
260 Table 1. Equations for the evaluation of diffusive flux as a function of averaging methods for
 261 interfacial properties.

	Flux equation	Averaged terms at the interface
Reference method	$J_{i,p}^x = -\overline{D}_{i,e} \frac{\Delta c_i}{\Delta x} + z_i \overline{D}_{i,e} \frac{\Delta c_i}{\Delta \ln c_i} \frac{\sum_j z_j \overline{D}_{j,e} \frac{\Delta c_j}{\Delta x}}{\sum_j z_j^2 \overline{D}_{j,e} \frac{\Delta c_j}{\Delta \ln c_j}}$	$c_i = \frac{\ln c_{i,1} - \ln c_{i,2}}{c_{i,1} - c_{i,2}}$ $\overline{D}_{i,e} = \frac{D_{i,e,2} D_{i,e,1} (\Delta x_2 + \Delta x_1)}{D_{i,e,2} \Delta x_1 + D_{i,e,1} \Delta x_2}$
Alternative method 1	$J_{i,p}^x = -\overline{D}_{i,e} \frac{\Delta c_i}{\Delta x} + z_i \overline{D}_{i,e} c_i \frac{\sum_j z_j \overline{D}_{j,e} \frac{\Delta c_j}{\Delta x}}{\sum_j z_j^2 \overline{D}_{j,e} c_j}$	$\overline{D}_{i,e} c_i = \frac{D_{e,2} c_{i,2} \Delta x_1 D_{e,1} c_{i,1} \Delta x_2}{D_{e,2} c_{i,2} \Delta x_1 + D_{e,1} c_{i,1} \Delta x_2}$ $\overline{D}_{i,e} = \frac{D_{i,e,2} D_{i,e,1} (\Delta x_2 + \Delta x_1)}{D_{i,e,2} \Delta x_1 + D_{i,e,1} \Delta x_2}$
Alternative method 2	$J_{i,p}^x = -\overline{D}_{i,e} \frac{\Delta c_i}{\Delta x} + z_i \overline{D}_{i,e} c_i \frac{\sum_j z_j \overline{D}_{j,e} \frac{\Delta c_j}{\Delta x}}{\sum_j z_j^2 \overline{D}_{j,e} c_j}$	$c_i = \frac{c_{i,1} \Delta x_1 + c_{i,2} \Delta x_2}{\Delta x_1 + \Delta x_2}$ $\overline{D}_{i,e} = \frac{D_{i,e,2} D_{i,e,1} (\Delta x_2 + \Delta x_1)}{D_{i,e,2} \Delta x_1 + D_{i,e,1} \Delta x_2}$

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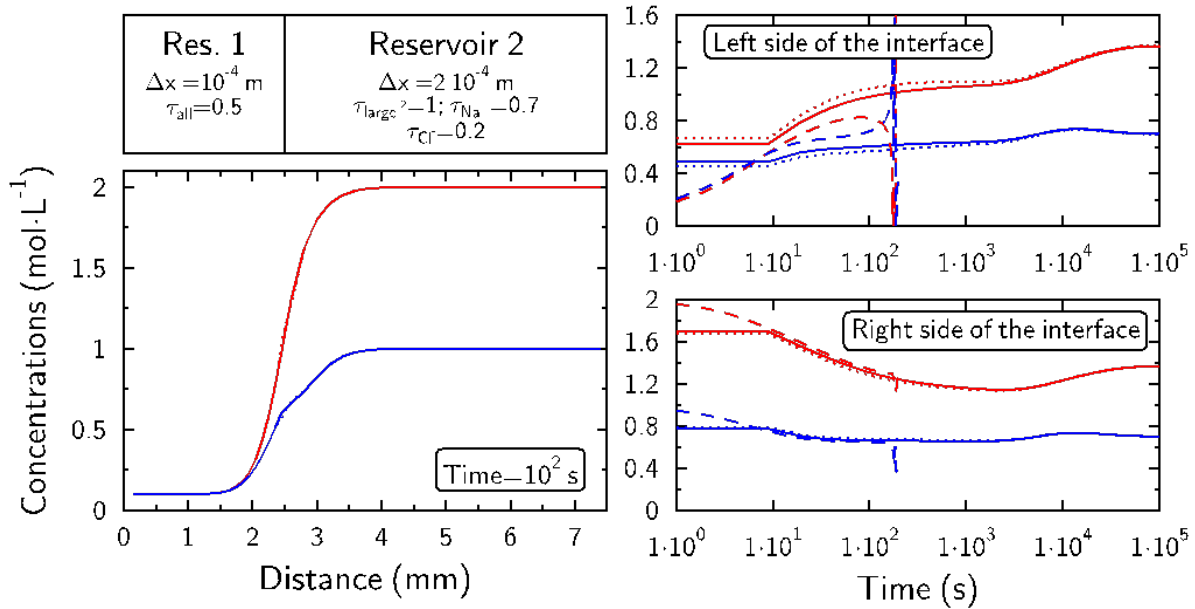
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266 **Figure 1.** Top left: system 1 under investigation. The gray area represents the membrane
 267 (thickness=200 μm) that separates the two reservoirs (length=5 mm each), and which is
 268 impermeable to the large anionic molecules. Initial Na^+ , Cl^- and large anionic molecule
 269 concentrations are indicated for each reservoir. Bottom left: Na^+ (red) and Cl^- (blue)
 270 concentration profiles obtained after 10^5 s of diffusion. The two circles at $x=8 \text{ mm}$ indicate the
 271 concentration expected in reservoir 2 according to Donnan equilibrium. Plain line: reference
 272 model. Dotted line: alternative model 2. Right: Na^+ (red) and Cl^- (blue) concentration on the left
 273 (top) and right (bottom) side of the membrane as a function of time and predicted with the
 274 different models. Plain line: reference model. Dashed line: alternative model 1. Dotted line:
 275 alternative model 2. Note that the calculation becomes unstable with the alternative model 1 after
 276 $\sim 300 \text{ s}$ of simulated time because of charge balance issues, and that electroneutrality was not
 277 achieved next to the membrane with the alternative model 2.

278



279

280 **Figure 2.** Top left figure: heterogeneous system 2 under investigation. Initial Na^+ , Cl^- are the
 281 same as in system 1. The large anionic molecule concentration was two times lower, while its
 282 charge was set to -2 instead of -1. Grid cell discretization and tortuosity factors are indicated in
 283 the figure. Bottom left figure: Na^+ (red) and Cl^- (blue) concentration profiles obtained after 100 s
 284 of diffusion. Plain line: reference model. Dotted line: alternative model 2. Right figure: Na^+ (red)
 285 and Cl^- (blue) concentration on the left (top) and right (bottom) side of the interface between the
 286 two reservoirs as a function of time and predicted with the different models. Plain line: reference
 287 model. Dashed line: alternative model 1. Dotted line: alternative model 2. Note that the
 288 calculation becomes unstable with the alternative model 1 after ~ 300 s of simulated time because
 289 of charge balance issues.

290 6 Conclusions

291 In the present study, the proper numerical method was defined to average the concentrations of
 292 dissolved species and the porous media properties at the interface between two grid cells in order
 293 to solve the Nernst-Planck equation with a finite difference/volume method. The computation of
 294 the weighted arithmetic average (alternative method 2) has been historically the averaging
 295 procedure that is used in most reactive transport codes that can solve the Nernst Planck
 296 equations. Our results emphasize the necessity to change this averaging method to one based on
 297 a logarithmic-differential average, *i.e.* the reference method demonstrated in the present study,
 298 and proposed previously by Gimmi and Alt-Epping (2018). The resulting improvement in the
 299 numerical stability and in the accuracy of concentration prediction is especially necessary to
 300 model semi-permeable membrane properties such as those used in water treatment processes.

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307 **References**

- 308 Anna, P. de, Le Borgne, T., Dentz, M., Bolster, D., Davy, P., 2011. Anomalous kinetics in
309 diffusion limited reactions linked to non-Gaussian concentration probability distribution
310 function. *The Journal of chemical physics* 135, 174104.
- 311 Anna, P. de, Jimenez-Martinez, J., Tabuteau, H., Turuban, R., Le Borgne, T., Derrien, M.,
312 Méheust, Y., 2013. Mixing and reaction kinetics in porous media: an experimental pore
313 scale quantification. *Environmental science & technology* 48, 508–516.
- 314 Appelo, C.A.J., 2017. Solute transport solved with the Nernst-Planck equation for concrete pores
315 with “free” water and a double layer. *Cement and Concrete Research* 101, 102–113.
- 316 Appelo, C.A.J., Van Loon, L.R., Wersin, P., 2010. Multicomponent diffusion of a suite of tracers
317 (HTO, Cl, Br, I, Na, Sr, Cs) in a single sample of Opalinus clay. *Geochimica et*
318 *Cosmochimica Acta* 74, 1201–1219.
- 319 Appelo, C.A.J., Vinsot, A., Mettler, S., Wechner, S., 2008. Obtaining the porewater composition
320 of a clay rock by modeling the in- and out-diffusion of anions and cations from an in-situ
321 experiment. *Journal of Contaminant Hydrology* 101, 67–76.
- 322 Appelo, C.A.J., Wersin, P., 2007. Multicomponent diffusion modeling in clay systems with
323 application to the diffusion of tritium, iodide, and sodium in Opalinus clay.
324 *Environmental Science & Technology* 41, 5002–5007.
- 325 La Bolle, E.M., Fogg, G.E., 2001. Role of molecular diffusion in contaminant migration and
326 recovery in an alluvial aquifer system. *Transport in Porous Media* 42, 155–179.
- 327 La Bolle, E.M., Fogg, G.E., Eweis, J.B., Gravner, J., Leaist, D.G., 2008. Isotopic fractionation by
328 diffusion in groundwater. *Water Resources Research* 44.
- 329 Bone, S.E., Cahill, M.R., Jones, M.E., Fendorf, S., Davis, J., Williams, K.H., Bargar, J.R., 2017.
330 Oxidative uranium release from anoxic sediments under diffusion-limited conditions.
331 *Environmental Science & Technology* 51, 11039–11047.
- 332 Le Borgne, T., Dentz, M., Davy, P., Bolster, D., Carrera, J., De Dreuzy, J.-R., Bour, O., 2011.
333 Persistence of incomplete mixing: A key to anomalous transport. *Physical Review E* 84,
334 015301.
- 335 Le Borgne, T., Dentz, M., Villermanx, E., 2013. Stretching, coalescence, and mixing in porous
336 media. *Physical review letters* 110, 204501.
- 337 Boudreau, B.P., Meysman, F.J., Middelburg, J.J., 2004. Multicomponent ionic diffusion in
338 porewaters: Coulombic effects revisited. *Earth and Planetary Science Letters* 222, 653–
339 666.
- 340 Bourg, I.C., Richter, F.M., Christensen, J.N., Sposito, G., 2010. Isotopic mass dependence of
341 metal cation diffusion coefficients in liquid water. *Geochimica et Cosmochimica Acta* 74,
342 2249–2256.
- 343 Bourg, I.C., Sposito, G., 2007. Molecular dynamics simulations of kinetic isotope fractionation
344 during the diffusion of ionic species in liquid water. *Geochimica et Cosmochimica Acta*
345 71, 5583–5589.
- 346 Bourg, I.C., Tournassat, C., 2015. Chapter 6 - Self-diffusion of water and ions in clay barriers.
347 In: Tournassat, C., Steefel, C.I., Bourg, I.C., Bergaya, F. (Eds.), *Natural and Engineered*
348 *Clay Barriers, Developments in Clay Science*. Elsevier, pp. 71–100.

- 349 Chapman, S.W., Parker, B.L., 2005. Plume persistence due to aquitard back diffusion following
350 dense nonaqueous phase liquid source removal or isolation. *Water Resources Research*
351 41.
- 352 Chiogna, G., Cirpka, O.A., Grathwohl, P., Rolle, M., 2011. Relevance of local compound-
353 specific transverse dispersion for conservative and reactive mixing in heterogeneous
354 porous media. *Water Resources Research* 47.
- 355 Alt-Epping, P., Gimmi, T., Wersin, P., Jenni, A., 2018. Incorporating electrical double layers
356 into reactive-transport simulations of processes in clays by using the Nernst-Planck
357 equation: A benchmark revisited. *Applied Geochemistry* 89, 1–10.
- 358 Alt-Epping, P., Tournassat, C., Rasouli, P., Steefel, C.I., Mayer, K.U., Jenni, A., Mäder, U.,
359 Sengor, S.S., Fernandez, R., 2015. Benchmark reactive transport simulations of a column
360 experiment in compacted bentonite with multispecies diffusion and explicit treatment of
361 electrostatic effects. *Computational Geosciences* 19, 535–550.
- 362 Felmy, A.R., Weare, J.H., 1991a. Calculation of multicomponent ionic diffusion from zero to
363 high concentration: I. The system Na-K-Ca-Mg-Cl-SO₄-H₂O at 25 C. *Geochimica et*
364 *Cosmochimica Acta* 55, 113–131.
- 365 Felmy, A.R., Weare, J.H., 1991b. Calculation of multicomponent ionic diffusion from zero to
366 high concentration: II. Inclusion of associated ion species. *Geochimica et Cosmochimica*
367 *Acta* 55, 133–144.
- 368 Giambalvo, E.R., Steefel, C.I., Fisher, A.T., Rosenberg, N.D., Wheat, C.G., 2002. Effect of
369 fluid-sediment reaction on hydrothermal fluxes of major elements, eastern flank of the
370 Juan de Fuca Ridge. *Geochimica et Cosmochimica Acta* 66, 1739–1757.
- 371 Gimmi, T., Alt-Epping, P., 2018. Simulating Donnan equilibria based on the Nernst-Planck
372 equation. *Geochimica et Cosmochimica Acta* 232, 1–13.
- 373 Glaus, M., Aertsens, M., Appelo, C., Kupcik, T., Maes, N., Van Laer, L., Van Loon, L., 2015.
374 Cation diffusion in the electrical double layer enhances the mass transfer rates for Sr²⁺,
375 Co²⁺ and Zn²⁺ in compacted illite. *Geochimica et Cosmochimica Acta* 165, 376–388.
- 376 Glaus, M.A., Birgersson, M., Karnland, O., Van Loon, L.R., 2013. Seeming steady-state uphill
377 diffusion of ²²Na⁺ in compacted montmorillonite. *Environmental Science & Technology*
378 47, 11522–11527.
- 379 Gouze, P., Melean, Y., Le Borgne, T., Dentz, M., Carrera, J., 2008. Non-Fickian dispersion in
380 porous media explained by heterogeneous microscale matrix diffusion. *Water Resources*
381 *Research* 44.
- 382 Gvirtzman, H., Gorelick, S., 1991. Dispersion and advection in unsaturated porous media
383 enhanced by anion exclusion. *Nature* 352, 793.
- 384 Hadley, P.W., Newell, C., 2014. The new potential for understanding groundwater contaminant
385 transport. *Groundwater* 52, 174–186.
- 386 Haghghi, E., Shahraeeni, E., Lehmann, P., Or, D., 2013. Evaporation rates across a convective
387 air boundary layer are dominated by diffusion. *Water Resources Research* 49, 1602–
388 1610.
- 389 Lasaga, A.C., 1979. The treatment of multi-component diffusion and ion pairs in diagenetic
390 fluxes. *American Journal of Science* 279, 324–346.
- 391 Liu, C., Shang, J., Zachara, J.M., 2011. Multispecies diffusion models: A study of uranyl species
392 diffusion. *Water Resources Research* 47.

- 393 Liu, C., Zachara, J.M., Yantasee, W., Majors, P.D., McKinley, J.P., 2006. Microscopic reactive
394 diffusion of uranium in the contaminated sediments at Hanford, United States. *Water*
395 *Resources Research* 42.
- 396 Marcus, A.K., Torres, C.I., Rittmann, B.E., 2010. Evaluating the impacts of migration in the
397 biofilm anode using the model PCBIOFILM. *Electrochimica Acta* 55, 6964–6972.
- 398 Muniruzzaman, M., Haberer, C.M., Grathwohl, P., Rolle, M., 2014. Multicomponent ionic
399 dispersion during transport of electrolytes in heterogeneous porous media: Experiments
400 and model-based interpretation. *Geochimica et Cosmochimica Acta* 141, 656–669.
- 401 Muniruzzaman, M., Rolle, M., 2015. Impact of multicomponent ionic transport on pH fronts
402 propagation in saturated porous media. *Water Resources Research* 51, 6739–6755.
- 403 Muniruzzaman, M., Rolle, M., 2016. Modeling multicomponent ionic transport in groundwater
404 with IPhreeqc coupling: Electrostatic interactions and geochemical reactions in
405 homogeneous and heterogeneous domains. *Advances in water resources* 98, 1–15.
- 406 Muniruzzaman, M., Rolle, M., 2017. Experimental investigation of the impact of compound-
407 specific dispersion and electrostatic interactions on transient transport and solute
408 breakthrough. *Water Resources Research* 53, 1189–1209.
- 409 Peeters, F., Beyerle, U., Aeschbach-Hertig, W., Holocher, J., Brennwald, M.S., Kipfer, R., 2002.
410 Improving noble gas based paleoclimate reconstruction and groundwater dating using
411 $^{20}\text{Ne}/^{22}\text{Ne}$ ratios. *Geochimica et Cosmochimica Acta* 67, 587–600.
- 412 Rasouli, P., Steefel, C.I., Mayer, K.U., Rolle, M., 2015. Benchmarks for multicomponent
413 diffusion and electrochemical migration. *Computational Geosciences* 1–11.
- 414 Robinet, J.-C., Sardini, P., Coelho, D., Parneix, J.-C., Prêt, D., Sammartino, S., Boller, E.,
415 Altmann, S., 2012. Effects of mineral distribution at mesoscopic scale on solute diffusion
416 in a clay-rich rock: Example of the Callovo-Oxfordian mudstone (Bure, France). *Water*
417 *Resources Research* 48, W05554.
- 418 Rolle, M., Chiogna, G., Bauer, R., Griebl, C., Grathwohl, P., 2010. Isotopic fractionation by
419 transverse dispersion: Flow-through microcosms and reactive transport modeling study.
420 *Environmental science & technology* 44, 6167–6173.
- 421 Rolle, M., Sprocati, R., Masi, M., Jin, B., Muniruzzaman, M., 2018. Nernst-Planck-based
422 description of transport, coulombic interactions, and geochemical reactions in porous
423 media: Modeling approach and benchmark experiments. *Water Resources Research* 54,
424 3176–3195.
- 425 Shackelford, C.D., 1991. Laboratory diffusion testing for waste disposal – A review. *Journal of*
426 *Contaminant Hydrology* 7, 177–217.
- 427 Steefel, C.I., Appelo, C.A.J., Arora, B., Jacques, D., Kalbacher, T., Kolditz, O., Lagneau, V.,
428 Lichtner, P.C., Mayer, K.U., Meeussen, J.C.L., Molins, S., Moulton, D., Shao, H.,
429 Šimunek, J., Spycher, N., Yabusaki, S.B., Yeh, G.T., 2015. Reactive transport codes for
430 subsurface environmental simulation. *Computational Geosciences* 19, 445–478.
- 431 Steefel, C.I., Maher, K., 2009. Fluid-rock interaction: A reactive transport approach. *Reviews in*
432 *Mineralogy and Geochemistry* 70, 485–532.
- 433 Tinnacher, R.M., Holmboe, M., Tournassat, C., Bourg, I.C., Davis, J.A., 2016. Ion adsorption
434 and diffusion in smectite: molecular, pore, and continuum scale views. *Geochimica et*
435 *Cosmochimica Acta* 177, 130–149.
- 436 Tokunaga, T.K., Shen, W., Wan, J., Kim, Y., Cihan, A., Zhang, Y., Finsterle, S., 2017. Water
437 Saturation Relations and Their Diffusion-Limited Equilibration in Gas Shale:

- 438 Implications for Gas Flow in Unconventional Reservoirs. *Water Resources Research* 53,
439 9757–9770.
- 440 Tournassat, C., Steefel, C.I., 2015. Ionic transport in nano-porous clays with consideration of
441 electrostatic effects. *Reviews in Mineralogy and Geochemistry* 80, 287–330.
- 442 Tournassat, C., Steefel, C.I., 2019a. Modeling diffusion processes in the presence of a diffuse
443 layer at charged mineral surfaces. A benchmark exercise. *Computational Geosciences*.
- 444 Tournassat, C., Steefel, C.I., 2019b. Reactive transport modeling of coupled processes in
445 nanoporous media. *Reviews in Mineralogy and Geochemistry* 85, 75–110.
- 446 Ben-Yaakov, S., 1972. Diffusion of sea water ions–I. Diffusion of sea water into a dilute
447 solution. *Geochimica et Cosmochimica Acta* 36, 1395–1406.
- 448 Zachara, J., Brantley, S., Chorover, J., Ewing, R., Kerisit, S., Liu, C., Perfect, E., Rother, G.,
449 Stack, A.G., 2016. Internal domains of natural porous media revealed: critical locations
450 for transport, storage, and chemical reaction. *Environmental Science & Technology* 50,
451 2811–2829.
- 452