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Multicomponent ionic transport modeling in physically and electrostatically heterogeneous porous media with PhreeqcRM coupling for geochemical reactions

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Key Points:

- Multi-continua-based formulation for multidimensional transport of charged species in clays and sandy-clayey systems
- Nernst-Planck diffusive/dispersive fluxes and geochemical reactions with PhreeqcRM
- Numerical experiments in 2-D physically and electrostatically heterogeneous domains at different scales

Abstract

Low-permeability aquitards, such as clay layers and inclusions, are of utmost importance for contaminant transport in groundwater systems. Although most dissolved species, contaminants, and clay surfaces are charged, the role of electrostatic interactions in subsurface flow-through systems has not been extensively investigated. This study presents a two-dimensional multicomponent reactive transport investigation of diffusive/dispersive and electrostatic processes in homogeneous and heterogeneous clay systems. The proposed approach is based on multiple continua and is capable to accurately describe charge interactions during ionic transport in the free water, diffuse layer, and interlayer water of charged porous media. The diffuse layer composition is simulated by considering a mean electrostatic potential following Donnan approach, whereas the interlayer composition is calculated by adopting the Gaines-Thomas convention. Diffusive/dispersive fluxes within each sub-continuum (free water, diffuse layer, and interlayer) are calculated solving the Nernst-Planck equation while maintaining a net zero-charge flux. Furthermore, the

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multidimensional flow and transport model is coupled with the geochemical code PHREEQC, by utilizing the PhreeqcRM module, thus enabling great flexibility to access all PHREEQC's reaction capabilities. The code is benchmarked in 1-D systems against other software and previously published experimental data. Successively, reactive transport simulations are performed in 2-D clayey-sandy flow-through domains with spatially variable physical and electrostatic properties at both laboratory and field scales. The results reveal that different properties of surface charge, diffuse layer, and Coulombic interactions impact the transport of charged species and lead to distinct spatial distribution of the ions in the different sub-continua and to significantly different breakthrough curves.

1 Introduction

Transport of charged species in low-permeability porous media such as clays and clay rocks is important in many natural geologic formations and engineering applications including the long-term disposal of radioactive wastes in geological repositories (e.g., Nagra, 2002; Pearson et al., 2003; Posiva, 2008), geologic carbon storage (e.g., Song & Zhang, 2013; Shao et al., 2014; Bourg et al., 2015), hydrogen storage and release (e.g., Oladyskin & Panfilov, 2011), shale gas exploration and shale weathering (e.g., Morrison et al., 2012; Vidic et al., 2013; Conley et al., 2016), oilfield applications (e.g., Anderson et al., 2010; Wilson & Wilson, 2014), and groundwater transport and remediation (e.g., Parker et al., 2008; Yang et al., 2015). One important characteristic of clays is the negatively charged surface which significantly affects the distribution and movement of porewater species (e.g., Birgersson & Karnland, 2009; Jougnet et al., 2009; Gimmi & Kosakowski, 2011; Glaus et al., 2013; Tinnacher et al., 2016; Tertre et al., 2018). The electrostatic forces exerted by the surface charge attract cations and repel anions, leading to the formation of a diffuse layer (DL) adjacent to the surface where anions are partly excluded and cations are enriched (e.g., Van Loon et al., 2007; Descostes et al., 2008; Tournassat & Appelo, 2011; Wigger & Van Loon, 2017; Wersin et al., 2018). Therefore, pore space in such clay systems can be characterized by a diffuse layer that counterbalances the surface charge, and a charge-balanced “bulk” or “free” water region unaffected by the mineral surface charge (e.g., Appelo & Wersin, 2007; Tournassat & Steefel, 2015; Charlet et al., 2017). The thickness and composition of the diffuse layer is dependent on the ionic strength of the free water solution (e.g., Appelo et al., 2008; Tournassat & Appelo, 2011; Soler et al., 2019). In addition to the diffuse layer, ions may also adsorb directly onto the Stern layer of the surface or to the interlayer (IL) space between individual TOT (tetrahedral-octahedral-tetrahedral) layers enabling ion-exchange like processes (e.g., Leroy & Revil, 2004; Leroy et al., 2006; Glaus et al., 2007; Appelo et al., 2010; Tertre et al., 2015; Bourg et al., 2017). Mass flux of a charged solute in such clayey media is not just dependent on its own properties or concentration gradient but it is a function of the physicochemical properties of clay, as well as the composition and charge of other dissolved species in the porewater solution (e.g., Appelo & Wersin, 2007; Tournassat & Appelo, 2011; Tournassat & Steefel, 2015; Alt-Epping et al., 2018). Thus, a formulation based on multiple continua, incorporating the charge driven processes in the diffuse layer, interlayer, Stern layer and free water, is required to rigorously and accurately describe mass transport (e.g., Appelo et al., 2008; 2010; Birgersson & Karnland, 2009; Jougnet et al., 2009; Steefel et al., 2015; Gimmi & Alt-Epping, 2018). Besides the surface-solute interactions, solute-solute Coulombic effects can also lead to considerable modification of the diffusive/dispersive fluxes of charged species to maintain local electroneutrality (e.g., Ben-Yaakov, 1972; Lasaga, 1979; Cussler, 2009). The latter has been found to be relevant not only in diffusion-dominated transport (e.g., Vinograd & McBain, 1941; Felmy & Weare,

1991; Giambalvo et al., 2002; Boudreau et al., 2004; Appelo & Wersin, 2007; Liu et al., 2011) but also under advection-dominated flow regimes in permeable porous media (e.g., Rolle et al., 2013a; Muniruzzaman et al., 2014; Muniruzzaman & Rolle, 2015; 2017).

Despite charge effects in porous media have been extensively explored in geochemical literature and their relevance on ionic transport is increasingly recognized, these processes are often ignored in solute transport simulations of subsurface flow systems. Only a few modeling frameworks can simulate coupled anion and cation transport influenced by charge induced electrostatic interactions (Meeussen, 2003; Parkhurst & Appelo, 2013; Rasouli et al., 2015; Steefel et al., 2015). When considering clay systems in continuum-scale reactive transport models, a multi-porosity approach is typically adopted where the total pore space of a clay rock is assumed to be composed of (i) a charge-free (or free, or bulk, or macro) porosity, (ii) a diffuse layer (or micro) porosity, and (iii) an interlayer porosity (e.g., Appelo et al., 2010; Tournassat & Steefel, 2015). The diffusive/dispersive fluxes in each of these porosities are described by the Nernst-Planck equation and the equilibrium between the free water (FW) and diffuse layer (DL) is calculated by Donnan equilibrium. Recently, a new approach solely based on the Nernst-Planck equation and with an implicit treatment of Donnan equilibria, has been proposed considering an explicit discretization of free and diffuse layer porosities that are assumed to be in diffusive exchange with each other (Gimmi & Alt-Epping, 2018). Furthermore, interlayer diffusion processes are rarely considered and only a few studies have addressed these processes (e.g., Appelo et al., 2010; Glaus et al., 2013). It is also worth noting that detailed investigations in clay systems are typically limited to centimeter scale samples and/or purely diffusion-controlled systems.

In this study we investigate the effects of charged surfaces and charge interactions during ionic transport at different scales, considering both diffusion- and advection-dominated conditions, as well as physical and electrostatic heterogeneity. We present a 2-D multicomponent reactive transport model for clay systems that is based on a multi-porosity formulation and explicitly takes into account the small-scale electrostatic processes originated from the surface and ions' charge. The code is called MMIT-Clay (Multidimensional Multicomponent Ionic Transport in Clay) and is able to describe coupled diffusive/dispersive solute movement including charge effects in free, diffuse layer, and interlayer porosities, activity gradient fluxes, advective transport in free porosity, and geochemical reactions. The diffuse layer composition is simulated by considering a mean electrostatic potential following Donnan approach, whereas the interlayer composition is calculated by adopting the Gaines-Thomas convention. Diffusive/dispersive fluxes within each individual sub-continuum (free water, diffuse layer, and interlayer) are calculated by solving the Nernst-Planck equation while maintaining a net zero-charge flux. The multidimensional reactive transport model is coupled with the geochemical code PHREEQC, by utilizing the PhreeqcRM module (Parkhurst & Wissmeier, 2015), which enables great flexibility to access all the PHREEQC's reaction capabilities. The developed code is benchmarked in 1-D systems by comparing the results with other software and experimental data from previous studies. Successively, reactive transport simulations are performed in 2-D clayey-sandy domains with spatially variable physical and electrostatic properties at two different scales representing laboratory flow-through setups and field-scale domains. The outcomes of the simulations are analyzed both in terms of breakthrough of the ions at the outlet of the domains and in terms of spatial distribution of the computed Nernst-Planck fluxes in the different sub-continua.

2 Methods

2.1 Multicomponent ionic transport: Concentrations and diffusive fluxes in free and charged porewater

Rigorous description of diffusive movement of charged species requires electrochemical migration to be included as a transport mechanism. In such electrolyte systems, charge-induced ion-ion interactions leads to the electrostatic coupling of ionic fluxes that results in a coordinated movement of positively and negatively charged species to maintain local charge balance (e.g., Ben-Yaakov, 1972). The relevance of these Coulombic effects has been explored in details under diffusion-dominated and macroscopic advection-dominated conservative and reactive transport conditions, which led to the development of multicomponent diffusion theories (e.g., Lasaga, 1979; Felmy & Weare, 1991; Giambalvo et al., 2002; Boudreau et al., 2004; Appelo & Wersin, 2007; Cussler, 2009; Liu et al., 2011) and the concept of multicomponent ionic dispersion (e.g., Rolle et al., 2013a; Muniruzzaman et al., 2014; Muniruzzaman & Rolle, 2015; 2017). Formulations of ionic diffusion are commonly based on the thermodynamic electrochemical potential (μ_i), rather than the concentration (e.g., Appelo & Wersin, 2007; Cussler, 2009):

$$\mu_i = \mu_i^0 + RT \ln a_i + z_i F \varphi \quad (1)$$

where μ_i^0 [J/mol] is the electrochemical potential at the standard state, R [J/mol/K] is the ideal gas constant, T [K] is the absolute temperature, a_i [-] is the activity of species i ($a_i = \gamma_i c_i / c^0$ with γ_i [-], c_i [mol/L], and c^0 [= 1 mol/kg H₂O, Appelo & Wersin, 2007], being the activity coefficient, concentration, and standard state, respectively), z_i [-] is the charge number, F [J/V/eq] is Faraday's constant, and φ [V] is the electrical potential.

The diffusive flux (J_i [mol/m²/s]) of a charged species i is derived from the spatial gradient in electrochemical potential:

$$J_i = -\frac{u_i c_i}{|z_i| F} \nabla \mu_i = -\frac{u_i R T}{|z_i| F} c_i \nabla (\ln a_i) - \frac{u_i}{|z_i|} c_i z_i \nabla \varphi \quad (2)$$

where, u_i [m²/s/V] is the mobility, which is related to the self-diffusion coefficient ($D_{aq,i}$ [m²/s]) of species i by $\frac{u_i R T}{|z_i| F} = D_{aq,i}$. Eq. (2) represents the Nernst-Planck equation for the flux of a charged species and can also be expressed as:

$$J_i = -D_{aq,i} \left(\nabla c_i + c_i \nabla \ln \gamma_i + \frac{z_i F}{R T} c_i \nabla \varphi \right). \quad (3)$$

By considering the activity gradients as:

$$c_i \nabla \ln \gamma_i = c_i \frac{\partial \ln \gamma_i}{\partial c_i} \nabla c_i = \frac{\partial \ln \gamma_i}{\partial \ln c_i} \nabla c_i, \quad (4)$$

the Nernst-Planck equation can be further rearranged to:

$$J_i = -D_{aq,i} \left(1 + \frac{\partial \ln \gamma_i}{\partial \ln c_i} \right) \nabla c_i - \frac{D_{aq,i} z_i F}{R T} c_i \nabla \varphi. \quad (5)$$

The electrical potential gradient ($\nabla \varphi$) can be calculated using the Poisson equation. However, in the absence of any external electric field, the null current condition ($I \equiv \sum_{i=1}^N z_i J_i = 0$) is valid and is considered in continuum descriptions of multicomponent ionic transport (e.g., Boudreau et al., 2004). Thus, $\nabla \varphi$ in Eq. (5) can be eliminated as an unknown by expressing this gradient term as:

$$\nabla \phi = - \frac{\sum_{i=1}^N \left[z_i D_{aq,i} \left(1 + \frac{\partial \ln \gamma_i}{\partial \ln c_i} \right) \nabla c_i \right]}{\frac{F}{RT} \sum_{i=1}^N (z_i^2 D_{aq,i} c_i)} \quad (6)$$

Upon substituting Eq. (6), the flux equation can be recast in terms of known parameters:

$$J_i = -D_{aq,i} \left(1 + \frac{\partial \ln \gamma_i}{\partial \ln c_i} \right) \nabla c_i + \frac{D_{aq,i} z_i c_i}{\sum_{j=1}^N (z_j^2 D_{aq,j} c_j)} \sum_{j=1}^N \left[z_j D_{aq,j} \left(1 + \frac{\partial \ln \gamma_j}{\partial \ln c_j} \right) \nabla c_j \right] \quad (7)$$

This formulation clearly demonstrates that the movement of a particular charged species is a function of concentration gradients, self-diffusion coefficients, activity coefficients, and charge numbers not only of that ion but also of all other charged species in solution.

In charged media such as clay or clay rocks, besides inter-ionic effects in solution, surface charge also induces an electrostatic potential field. At the surface-water interface, typically known as diffuse layer (DL), the distribution of ions is characterized by a gradual increase of counter-ions and decrease of co-ions along the distance perpendicular to the surface (e.g., Sposito, 1992; Tournassat & Steefel, 2015). At the pore scale, these electrostatic effects can be modeled by the modified Gouy-Chapman (MGC) model, based on the Poisson-Boltzmann equation, which suggests a Boltzmann distribution of ionic concentrations in the diffuse layer (e.g., Tournassat & Appelo, 2011). However, incorporation of the full Poisson-Boltzmann approach in continuum scale reactive transport codes is too computationally demanding and often impractical, hence, a Donnan approach (Donnan & Guggenheim, 1932) is a viable alternative that is often adopted in simulations involving charged media (e.g., Muurinen et al., 2004; Appelo & Wersin, 2007; Birgersson & Karnland, 2009; Appelo et al., 2010; Gimmi & Alt-Epping, 2018; Soler et al., 2019). In this approach, the pore space is conceptualized by subdividing it into two sub-continua: a charge-neutral “free” porewater (or “bulk” water), and a charged “Donnan” porewater (containing diffuse layer). Instead of considering spatial distribution of electrostatic potential along the diffuse layer, an average (Donnan) potential is considered, linking the concentrations in these porosities as:

	$c_i^{DL} = \Gamma_i c_i \exp \left(\frac{-z_i F \phi^{DL}}{RT} \right) = \Gamma_i c_i g_i^{DL} \quad (8)$	
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where c_i^{DL} [mol/L] is the concentration of species i in the Donnan space, Γ_i [-] is the ratio of the activity coefficients in free and Donnan water ($= \gamma_i / \gamma_i^{DL}$) (typically assumed to be 1 in most reactive transport codes, Appelo & Wersin, 2007; Tournassat & Steefel, 2015), ϕ^{DL} [V] is the mean Donnan potential, and g_i^{DL} represents the so called Boltzmann factor or enrichment factor in the Donnan water.

It has been shown previously that the electrochemical potential gradient in the diffuse layer is equal to the chemical potential gradient in the free porewater (Appelo & Wersin, 2007; Jougnot et al., 2009). Thus, the same Nernst-Planck equation describing the ionic flux through free porosity also applies to the Donnan water:

$$J_i^{DL} = -D_{aq,i}^{DL} \left(1 + \frac{\partial \ln \gamma_i^{DL}}{\partial \ln c_i^{DL}} \right) \nabla c_i^{DL} + \frac{D_{aq,i}^{DL} z_i c_i^{DL}}{\sum_{j=1}^N (z_j^2 D_{aq,j}^{DL} c_j^{DL})} \sum_{j=1}^N \left[z_j D_{aq,j}^{DL} \left(1 + \frac{\partial \ln \gamma_j^{DL}}{\partial \ln c_j^{DL}} \right) \nabla c_j^{DL} \right] \quad (9)$$

where γ_i^{DL} [-] is the activity coefficient in the Donnan water, and $D_{aq,i}^{DL}$ [m²/s] is the self-diffusion coefficient in Donnan water.

Unlike diffuse layer, ions within the interlayer space interact with the surface by exchange reactions, which is typically described within the framework of ion exchange theory (e.g., Gaines Thomas, 1953). Following the Gaines Thomas convention, which is the most popular one in geochemical and reactive transport calculations, the general exchange reactions between two cations are written as (Appelo, 1996):

where X^- is the sum of the exchangeable interlayer surface sites typically known as cation exchange capacity (CEC). Now, the concentration of an ionic species, i in the interlayer can be described by (Appelo, 1996; Parkhurst & Appelo, 2013),

$c_i^{IL} = \frac{CEC}{z_i} \beta_i = \left[\frac{CEC}{z_i} \left(\frac{K_{i/j} \beta_j^{1/z_j}}{c_j^{1/z_j}} \right)^{z_i} \right] c_i = g_i^{IL} c_i$	(11)
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where c_i^{IL} [mol/L] is the concentration of species i in the interlayer porosity, CEC [eq/L] is the exchange capacity, β_i, β_j [-] are the equivalent fractions, $K_{i/j}$ [-] is the exchange coefficient of species i with respect to species j , and g_i^{IL} refers to the enrichment factor in the interlayer water. Following a similar approach, diffusion of the interlayer species can also be expressed by the Nernst-Planck equation (Parkhurst & Appelo, 2013):

$$J_i^{IL} = -D_{aq,i}^{IL} \left(1 + \frac{\partial \ln \gamma_i^{IL}}{\partial \ln c_i^{IL}} \right) \nabla c_i^{IL} + \frac{D_{aq,i}^{IL} z_i c_i^{IL}}{\sum_{j=1}^N (z_j^2 D_{aq,j}^{IL} c_j^{IL})} \sum_{j=1}^N \left[z_j D_{aq,j}^{IL} \left(1 + \frac{\partial \ln \gamma_j^{IL}}{\partial \ln c_j^{IL}} \right) \nabla c_j^{IL} \right] \quad (12)$$

where $D_{aq,i}^{IL}$ [m²/s] is the self-diffusion coefficient in interlayer water, and γ_i^{IL} [-] is the activity coefficient of the exchange species. By collecting the like terms, the flux equations for free, Donnan, and interlayer water (Eqs. 7, 9, and 12) can be further rearranged in a more compact notation that takes the form:

$J_i^{\varsigma} = - \sum_{j=1}^N \left[D_{ij}^{\varsigma} \left(1 + \frac{\partial \ln \gamma_j^{\varsigma}}{\partial \ln c_j^{\varsigma}} \right) \nabla c_j^{\varsigma} \right]$	(13)
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where, superscript ς (= FW, DL, or IL) indicates the respective parameters in a particular domain of interest (i.e., free, Donnan, or interlayer porosity). D_{ij}^{ς} is the inter-diffusion coefficient, which includes both the pure diffusive and the electromigration flux components (Eq. 3), defined as:

$$D_{ij}^{\varsigma} = \delta_{ij} D_i^{\varsigma} - \frac{z_i z_j D_{aq,i}^{\varsigma} D_{aq,j}^{\varsigma} c_i^{\varsigma}}{\sum_{j=1}^N (z_j^2 D_{aq,j}^{\varsigma} c_j^{\varsigma})} \quad (14)$$

where, δ_{ij} is the Kronecker delta function, which is equal to 1 when $i=j$ and equal to 0 if $i \neq j$.

2.2 Equation for flow and transport in homogeneous and heterogeneous clay systems

In this study we consider flow and transport in heterogeneous porous media. The governing equation for steady-state flow in saturated porous media is expressed as (Cirpka et al., 1999a):

$$\nabla \cdot (\mathbf{K} \nabla h) = 0 \quad (15)$$

$$\nabla \cdot (\mathbf{K}^{-1} \nabla \psi) = 0$$

where, h [m] is the hydraulic head, ψ [m²/s] is the stream function, and $\mathbf{K}$ [m/s] is the hydraulic conductivity tensor. In heterogeneous flow-through systems the numerical solution of the flow problem is a necessary pre-requisite to solve solute transport.

In porous media, containing charged surfaces, where the dissolved porewater species are effectively partitioned among three sub-continua (free, Donnan, and interlayer porosity), the governing equation involving multicomponent ionic transport, electrostatic interactions, and chemical reactions can be written as:

$$\theta \left[\frac{\partial}{\partial t} (f^{FW} c_i) + \frac{\partial}{\partial t} (f^{DL} c_i^{DL}) + \frac{\partial}{\partial t} (f^{IL} c_i^{IL}) \right] = -\mathbf{q} \cdot \nabla c_i + \theta (\nabla \cdot \mathbf{J}_i^{Tot, All}) - \sum_{r=1}^{N_r} \nu_{ir} R_r \quad (16)$$

where θ [-] is the total porosity, f^{FW} , f^{DL} , f^{IL} [-] represent the fractions of the total porosity occupied by the free, Donnan and interlayer water respectively, t [s] is time, $\mathbf{q}$ [m/s] is the specific discharge vector, $\mathbf{J}_i^{Tot, All}$ [mol/m²/s] is the vector of total fluxes in all porosities, R_r [mol/m²/s] is the reactive source/sink term, and ν_{ir} [-] is the stoichiometric coefficient of species i for r -th reaction. In presence of advection in free porosity, the entries of $\mathbf{J}_i^{Tot, All}$ are derived following the approach formally equivalent to Eqs. (7, 9, 12-14) but replacing the self-diffusion coefficients by the hydrodynamic dispersion coefficients for free porewater and pore-diffusion coefficients for Donnan and interlayer porosities (e.g., Appelo et al., 2010; Muniruzzaman & Rolle, 2016; Rolle et al., 2018). Furthermore, these flux components can also be expressed only in terms of free water concentrations (c_i) by using the constitutive relationships in Eqs. (8) and (11). Thus, employing these substitutions and simplifications, $\mathbf{J}_i^{Tot, All}$ can be expressed in a two-dimensional local coordinate system (x_L , x_T), oriented along the principal flow direction, as:

$$\mathbf{J}_i^{Tot, All} = \begin{bmatrix} J_{L,i}^{Tot, All} \\ J_{T,i}^{Tot, All} \end{bmatrix} = \begin{bmatrix} f^{FW} J_{L,i}^{FW} + f^{DL} J_{L,i}^{DL} + f^{IL} J_{L,i}^{IL} \\ f^{FW} J_{T,i}^{FW} + f^{DL} J_{T,i}^{DL} + f^{IL} J_{T,i}^{IL} \end{bmatrix} = \begin{bmatrix} -\sum_{j=1}^N \left(\mathbf{D}_{L,ij}^{Tot, All} \left(1 + \frac{\partial \ln \gamma_j}{\partial \ln c_j} \right) \frac{\partial c_j}{\partial x_L} \right) \\ -\sum_{j=1}^N \left(\mathbf{D}_{T,ij}^{Tot, All} \left(1 + \frac{\partial \ln \gamma_j}{\partial \ln c_j} \right) \frac{\partial c_j}{\partial x_T} \right) \end{bmatrix} \quad (17)$$

where, the subscript L and T refer to the longitudinal and transverse components of the flux, respectively, and $\mathbf{D}_{L,ij}^{Tot, All}$ and $\mathbf{D}_{T,ij}^{Tot, All}$ are the matrices of longitudinal and transverse cross-coupled dispersion coefficients, respectively, which allow accounting for the flux of a charged species driven by both its own concentration and activity gradient and the electrical field created by inter-ionic and surface-solution interactions. These cross-coupled dispersion terms, formally analogous to inter-diffusion coefficients in Eq. (14), are expressed as:

$$\begin{aligned} \mathbf{D}_{L,ij}^{Tot, All} &= \delta_{ij} D_{L,i}^{Tot, All} - \frac{z_i z_j D_{L,i}^{Tot, All} D_{L,j}^{Tot, All} c_i}{\sum_{j=1}^N (z_j^2 D_{L,j}^{Tot, All} c_j)} \\ \mathbf{D}_{T,ij}^{Tot, All} &= \delta_{ij} D_{T,i}^{Tot, All} - \frac{z_i z_j D_{T,i}^{Tot, All} D_{T,j}^{Tot, All} c_i}{\sum_{j=1}^N (z_j^2 D_{T,j}^{Tot, All} c_j)} \end{aligned} \quad (18)$$

where $D_{L,i}^{Tot, All}$ and $D_{T,i}^{Tot, All}$ are the overall hydrodynamic self-dispersion coefficients (i.e., when a particular ion is “liberated” from the other charged species in solution) in the entire pore

space (i.e., including free, Donnan and interlayer) along the longitudinal and transverse directions,

$$\begin{aligned} D_{L,i}^{Tot,All} &= f^{FW} D_{L,i}^{FW} + f^{DL} D_{P,i}^{DL} g_i^{DL} + f^{IL} D_{P,i}^{IL} g_i^{IL} \\ D_{T,i}^{Tot,All} &= f^{FW} D_{T,i}^{FW} + f^{DL} D_{P,i}^{DL} g_i^{DL} + f^{IL} D_{P,i}^{IL} g_i^{IL} \end{aligned} \quad (19)$$

with $D_{L,i}^{FW}$ and $D_{T,i}^{FW}$ [m²/s] being the self-dispersion coefficients in the free porosity, and $D_{P,i}^{DL}$ and $D_{P,i}^{IL}$ [m²/s] being the self-pore-diffusion coefficients in the Donnan and interlayer porosities, respectively. The hydrodynamic dispersion coefficients are important for the accurate description of dispersive transport in free porosity and can be parameterized with a linear relationship for the longitudinal component (Guedes de Carvalho & Delgado, 2005; Kurotori et al., 2019) and with a non-linear compound-specific relationship (Chiogna et al., 2010; Rolle et al., 2012; Hochstelter et al., 2013) for the transverse component:

$$\begin{aligned} D_{L,i}^{FW} &= D_{P,i}^{FW} + 0.5vd \\ D_{T,i}^{FW} &= D_{P,i}^{FW} + D_{aq,i}^{FW} \left(\frac{Pe_i^2}{Pe_i + 2 + 4\delta^2} \right)^\beta \end{aligned} \quad (20)$$

where, d [m] is the average grain size diameter, v [m/s] is the average flow velocity in free water, Pe_i [-] ($=vd/D_{aq,i}$) is the grain Péclet number, δ [-] is the ratio between the length of a pore channel to its hydraulic radius, β [-] is an empirical exponent that accounts for the effects of incomplete mixing in the pore channels. A comprehensive analysis of transverse dispersion datasets in two-dimensional and three-dimensional setups has provided average values of $\delta=5.37$ and $\beta=0.5$ (Ye et al., 2015a). The velocity-independent pore diffusion term can be expressed as: $D_{P,i}^\varsigma = D_{aq,i}/\tau^\varsigma$, where τ^ς ($=\tau^{FW}$, τ^{DL} , or τ^{IL}) [-] is the tortuosity in each individual sub-domain.

In heterogeneous domains, a spatially variable description of local hydrodynamic self-dispersion coefficients and self-pore-diffusion coefficients is of critical importance for accurate simulation of multicomponent ionic transport. Therefore, high-resolution transport simulations in such domains require a heterogeneous description of the grain diameter (d , in Eq. 20) by considering a direct link to the local hydraulic conductivity. MMIT-Clay uses the simple Hazen approximation (Hazen, 1892), which was adopted in previous studies of transport in heterogeneous systems (e.g., Eckert et al., 2012; Rolle et al., 2013b):

$$d \approx c\sqrt{K} \quad (21)$$

where, $c = 0.01 \text{ m}^{0.5} \text{ s}^{0.5}$ is an empirical proportionality constant. This approach ensures a greatly improved representation of local dispersion compared to the common practice of considering constant dispersivities in heterogeneous formations.

2.2.1 Calculation of enrichment factors

The Boltzmann factor (g_i^{DL}), which is a function of Donnan potential (ϕ_{DL}), in Eq. (8) is calculated by solving locally the charge balance equation in Donnan space (Appelo and Wersin, 2007):

$$V_{DL} \sum_{i=1}^N z_i c_i^{DL} + Su = 0 \quad (22)$$

where, V_{DL} [L] is the volume of Donnan space, and Su [mol] is surface charge. For only oppositely charged species with the same charge number, this equation results in a quadratic form (e.g., Birgersson and Karnland, 2009; Appelo, 2017):

$$(g_i^{DL})^2 + \frac{Su}{0.5V_{DL} \sum_{i=1}^N (|z_i|c_i)} g_i^{DL} - 1 = 0 \quad (23)$$

with the solution:

$$g_i^{DL} = -\frac{Su}{V_{DL} \sum_{i=1}^N (|z_i|c_i)} + \sqrt{\left(\frac{Su}{V_{DL} \sum_{i=1}^N (|z_i|c_i)}\right)^2 + 1} \quad (24)$$

In interlayer water, the enrichment factor (Eq. 11) is calculated by expressing equivalent fractions (β_i) for all species as a function of the equivalent fraction for the “reference” species (j in Eq. 11), which is typically assumed to be Na^+ in geochemical codes such as PHREEQC (e.g., Appelo & Postma, 2005; Parkhurst & Appelo, 2013). Thus, the equivalent fractions are calculated by solving,

$$\sum_{i=1}^N \beta_i = \sum_{i=1}^{N-1} \left(\frac{K_{i/j} \beta_j^{1/z_j}}{c_j^{1/z_j}} \right)^{z_i} c_i + \beta_j = 1 \quad (25)$$

2.2.2 Calculation of Donnan layer thickness

Although fixed thickness of Donnan layer is frequently used in reactive transport studies (e.g., Appelo et al., 2008; Alt-Epping et al., 2015), a more rigorous description requires the dependence of diffuse layer dimensions on the ionic strength of the solution and can be represented in terms of Debye lengths:

$$\kappa^{-1} = \sqrt{\frac{\epsilon_0 \epsilon_w RT}{2 \cdot 10^3 F^2 I}} \quad (26)$$

where, κ^{-1} [m] is the Debye length, ϵ_0 [C²/J/m] is the permittivity of vacuum, ϵ_w [-] is the relative dielectric constant of water, and I [mol/L] is the ionic strength. In PHREEQC, the Donnan layer thickness is calculated by assuming a cylindrical shape of the total pore space, where the fractions of the free and Donnan porosity are dynamically calculated as (Appelo & Wersin, 2007; Appelo, 2017):

$$f^{FW} = \left(1 - \frac{n_D \kappa^{-1}}{r} \right)^2 \quad (27)$$

where n_D [-] is the number of Debye lengths, and r [m] is the radius of the cylindrical pore space (typically calculated as $r = 2V_{Tot}/A_s$ with V_{Tot} [m³] and A_s [m²] being the total pore volume and charged surface area) and $f^{FW} + f^{DL} + f^L = 1$. In MMIT-Clay we also adopt this approach in order to allow a direct comparison with the PHREEQC calculations, whereas a linear relation between the Donnan porosity and the Debye length ($f^{DL} = A_s n_D \kappa^{-1} / \theta$), as used in other studies (e.g., Soler et al., 2019) can also be easily implemented in the model.

2.2.3 Calculation of the activity gradient fluxes

In MMIT-Clay, we incorporate the same activity models adopted in PHREEQC to calculate the flux component due to the gradients of activity coefficients. For charged species PHREEQC uses either WATEQ Debye-Hückel (Truesdell & Jones, 1974) equation when ion-size (Debye-Hückel) parameters are given or Davies equation when such parameters are not available, whereas it uses Setchenow equation for the uncharged species (Parkhurst & Appelo, 2013):

$$\log \gamma_i = \begin{cases} -Az_i^2\sqrt{I}/\left(1+B^{\circ}a\sqrt{I}\right)+b_iI & \text{(if Debye-Hückel parameters are available)} \\ -Az_i^2\left(\sqrt{I}/\left(1+\sqrt{I}\right)-0.3I\right) & \text{(if Debye-Hückel parameters are unavailable)} \\ 0.1I & \text{(for uncharged species)} \end{cases} \quad (28)$$

With these activity models, we analytically calculate the partial derivatives in Eqs. (7, 9, 12, and 17) as,

$$\frac{\partial \ln \gamma_i}{\partial \ln c_i} = \begin{cases} 0.5c_i \ln(10) \left[-Az_i^4 / \left\{ 2\sqrt{I} \left(1 + B^{\circ}a\sqrt{I} \right)^2 \right\} + b_i z_i^2 \right] \\ 0.5c_i \ln(10) \left[-Az_i^2 \left[z_i^2 / \left\{ 2\sqrt{I} \left(1 + \sqrt{I} \right)^2 \right\} - 0.3 \right] \right] \\ 0 \end{cases} \quad (29)$$

This analytical approach is convenient because it eliminates the need for the numerical evaluation of $\nabla \ln \gamma_i$ and allows the quantification of activity gradient fluxes.

2.3 Modeling approach

The water flow through 2-D porous media (Eq. 15) is numerically solved with a finite element method (FEM) on a rectangular grid adopting bilinear quadrilateral elements (Cirpka, 1999b). In contrast, the multicomponent ionic transport is solved by finite volume method (FVM) on streamline-oriented grids, with quadrilateral elements oriented along the flow direction, which are constructed based on the results of the flow simulations (Cirpka et al., 1999a). Furthermore, the presented multicomponent ionic transport code (MMIT-Clay) is coupled with PHREEQC (Parkhurst & Appelo, 2013), taking advantage of the capabilities of linking this geochemical simulator with transport codes (Charlton & Parkhurst, 2011; Wissmeier & Barry, 2011; Nardi et al., 2014; He et al., 2015; Parkhurst & Wissmeier, 2015). MMIT-Clay utilizes the PhreeqcRM module (Parkhurst & Wissmeier, 2015), which allows great flexibility and a multi-purpose framework to access all the PHREEQC's reaction capabilities (e.g., Jara et al. 2017; Healy et al., 2018; Rolle et al. 2018). At the end of the advective and dispersive transport within a time step (Δt), the concentration vector of all the species (primary and secondary species from aqueous speciation) is passed to PhreeqcRM to perform reaction calculations (i.e., any other reactions excluding Donnan and/or interlayer processes), which are done by considering a batch reactor in each cell of the simulation domain containing user-defined reactive processes of interest. The newly updated concentrations from PhreeqcRM are passed back to the transport model in a subsequent time step (Fig. 1). A small length of the time step is recommended to reduce numerical errors associated with the operator-splitting step. Note that under the simplified assumption of immobile Donnan and interlayer water, it is also possible to simulate transport only within free porosity, and all the Donnan and interlayer calculations can be solved with PHREEQC. However, to consider mobile Donnan and interlayer species (diffusion in these porosities), exchange within these sub-continua must be solved externally to PHREEQC.

3 Benchmark Problems

The capability of the proposed multicomponent reactive transport model is systematically benchmarked by comparing the model outcomes with PHREEQC and previously published experimental data from diffusion and flow-through experiments in clay

samples. In particular, we consider selected benchmark problems to validate the implementation of specific features of the code:

- Benchmark 1: Donnan equilibrium and diffusion within Donnan water
- Benchmark 2: Donnan calculations compared to an experimental dataset
- Benchmark 3: Interlayer equilibrium and diffusion within interlayer water
- Benchmark 4: Interlayer equilibrium and diffusion compared to an experimental dataset
- Benchmark 5: Advection-diffusion calculations involving Donnan water, Stern layer and mineral dissolution-precipitation reactions.

Benchmark problem 1 shows the simulation involving simultaneous diffusion within free and Donnan porosity in a 1-D domain, and comparison with the analogous PHREEQC results. Subsequently, in Benchmark 2 diffusion calculation within the Donnan space is further verified against a diffusion-cell experiment performed by Tachi and Yotsuji (2014). In analogous setups, Benchmark problems 3 and 4 test the interlayer diffusion calculations by comparing the model outcomes with PHREEQC and with the experimental results from Glaus et al. (2013), respectively. Finally, in Benchmark 5, we consider a multicomponent advective-diffusive problem including both EDL and exchangeable surface charge along with mineral dissolution-precipitation reactions (component problem 5 of Alt-Epping et al., 2015). These tests allowed us to directly assess the capability of Donnan equilibrium, diffusion through Donnan space, interlayer equilibrium, interlayer diffusion, activity gradient fluxes, and coupling of the transport code with PhreeqcRM. Among these benchmark problems, we only show the results of Benchmark 2, 4, and 5 in this section, whereas problem 1 and 3 are described in the Supporting Information. Schematic diagrams of the setups used in different benchmarks are also presented in the Supporting Information (Fig. S1). Table 1 reports the input parameters for the benchmark problems presented in the following sections.

3.1 Through-diffusion experiments in montmorillonite plug (Benchmark 2)

In Benchmark 2, we compare our modeling approach with a dataset collected from through-diffusion experiments in a montmorillonite plug using anionic ($^{125}\text{I}^-$), cationic ($^{22}\text{Na}^+$, $^{137}\text{Cs}^+$), and neutral (HTO) tracers (Tachi & Yotsuji, 2014). The experimental setup includes a through-diffusion cell, in which a compacted clay sample is in contact with two reservoirs. At $t = 0$, the tracer species are loaded at the inlet reservoir, and they diffuse through the clay with time. The concentrations in both reservoirs are measured periodically during the experiment. The geometry, properties of the clay plug, and the simulation parameters are reported in Table 1 (second column).

Experimental results (markers) for different tracers and their comparison with the numerical simulations (lines) are plotted in Figure 2. At the inlet reservoir, tracer concentrations decrease as a function of time due to the diffusive transport through the clay (left axes in top row panels, red lines/markers). The breakthrough curves at the outlet reservoir show an increasing trend for all species (right axes in top row panels, blue lines/markers). This behavior is confirmed by the spatial profiles, which show the formation of concentration gradients within the clay sample (Fig. 2e-f).

Among the tracers, cations (especially Cs^+) are extremely enriched in the clay plug (Fig. 2g-h) compared to the neutral and anionic species. This behavior is a clear influence of the surface charge and it is observable also from the temporal profiles in the reservoirs, which show more pronounced decrease in the inlet reservoir and increase in the outlet reservoir for the cation concentrations (Fig. 2d). The experimentally measured temporal and spatial

profiles are simultaneously reproduced by considering a multi-continua conceptual model involving diffusive transport through free and diffuse layer water. A similar approach was also used by Tournassat and Steefel (2015) to benchmark their model with the same dataset. Half of the porosity (0.722) was attributed to the Donnan water, which was assumed to screen 90% of the total surface charge (1 eq/kg). The remaining 10% CEC was assumed to be balanced by the exchangeable species. The excellent agreement between the MMIT-Clay simulations and the experimental data validates the correct implementation of Donnan equilibrium and diffusion in Donnan space in the proposed model.

3.2 Through-diffusion experiments under a salinity gradient (Benchmark 4)

In problem 4, we benchmark the interlayer diffusion capability of MMIT-Clay against the experimental data provided by Glaus et al. (2013). The experimental setup is similar to the one used in problem 2. A salinity gradient was established within the montmorillonite plug by contacting it to two reservoirs containing 0.1 and 0.5 M NaClO₄ solutions. After reaching a linear concentration gradient, the experiment started by spiking ²²Na⁺ in both reservoirs at identical concentration. The experiments were performed in two clay plugs with lengths of 5 mm (Fig. 3a,c) and 10 mm (Fig. 3b,d) and reservoir volumes of 250 and 100 mL, respectively. The experimental details can be found in Glaus et al. (2013) and the input parameters for the simulations are listed in Table 1 (third column).

In both experiments, the measured concentration of ²²Na⁺ shows an increasing trend over time at 0.5 M reservoir (blue markers/lines) and a decreasing trend at 0.1 M reservoir (red markers/lines) even though ²²Na⁺ concentration was initially identical in both reservoirs (Fig. 3a,b). Such behavior is clearly indicative of “uphill” diffusion as also confirmed by the measured spatial profiles, which suggest the diffusive transport of ²²Na⁺ from the 0.1 M reservoir to the 0.5 M reservoir against the concentration gradient of the background electrolyte NaClO₄ (Fig. 3c,d). This behavior cannot be explained by classical Fickian diffusion, and Glaus et al. (2013) concluded that the concentration gradient of exchangeable cations within the clay nanopores are the dominant force for such outcome. They were able to reproduce the temporal profiles using an interlayer diffusion model implemented in PHREEQC. In this example, we also simulate these experiments by considering interlayer diffusion and by following the approach presented in section 2. In the clay, almost the entire porosity (0.30) was assigned to the interlayer, and only a very small value was set to free water porosity (~0.02). We also explicitly considered the filters at both ends of the clay sample by assuming a porosity of 0.32 and tortuosity of 6.67. The excellent agreement between the simulated and experimental temporal and spatial profiles effectively validates the interlayer calculations of MMIT-Clay.

3.3 Reactive transport in a bentonite core (Benchmark 5)

Benchmark problem 5 represents advective-diffusive transport of ionic species through a bentonite core in the presence of mineral dissolution-precipitation reactions. This problem was originally designed based on a flow-through experiment reported in previous studies (Karnland et al., 2009; Fernández et al., 2011; Mäder et al., 2012) and has been described in details in Alt-Epping et al. (2015). The setup includes a 5 cm long column, which is flushed by an influent solution with a constant influx of $2.3 \times 10^{-9} \text{ m}^3/(\text{m}^2\text{s})$ that is equivalent to a flow velocity of 1.016 m/y. In addition to the negatively charged montmorillonite, the solid materials contained calcite, gypsum, quartz, and K-feldspar. The detailed mineralogy, the mineral reactions, the composition of the inflow and initial solutions,

the surface reaction constants, and the thermodynamic database can be found in Alt-Epping et al. (2015). The total porosity (0.476) was divided into a free porosity (0.071) and a diffuse layer porosity (0.405), and the cation exchange capacity (*CEC*) of the surface was assumed to be compensated by 90% DL charge and 10% fixed charge at Stern layer (exchangeable species). The surface reactions in the latter are provided in Table 9 of Alt-Epping et al. (2015). Notice that these reactions can be simulated utilizing the coupling with PhreeqcRM. Fig. 4 shows the results obtained from the simulations performed with MMIT-Clay (lines) and with PHREEQC (markers). In the MMIT-Clay formulation, DL and Stern layer calculations were performed by solving equations (16-32), whereas the mineral reactions and aqueous speciation were performed by coupling with PhreeqcRM as explained in section 2.3. Also in this example, an excellent agreement exists between the simulated breakthrough curves (Fig. 4a), free water (Fig. 4b), diffuse layer (Fig. 4c), and Stern layer (Fig. 4d) compositions from these two codes.

4 Results and Discussion

In this section we investigate and discuss the impact of charged surfaces during multicomponent ionic transport, by means of numerical simulations, in 2-D physically and electrostatically heterogeneous sandy-clayey domains at different scales. We consider: (i) a meter-scale domain representative of a typical laboratory flow-through chamber, and (ii) a field-scale domain representing a vertical cross-section of an aquifer.

4.1 Transport in a lab-scale heterogeneous sandy-clayey domain

To investigate the relevance of electrostatic effects induced by the clay surfaces during multidimensional ionic transport in a flow-through setup, we performed numerical experiments by considering a 2-D domain with dimensions of 80 cm $\times$ 12 cm ($L \times H$). Such setup is representative of laboratory bench-scale experiments carried out in quasi 2-D flow-through chambers to study conservative and reactive transport in porous media (e.g., Tartakovsky et al., 2008; Bauer et al., 2009; Rolle et al., 2009; Haberer et al., 2013, 2015; Battistel et al. 2019). The domain involves a rectangular inclusion of clay material (20 cm $\times$ 2 cm) placed at the center of the sandy matrix. We considered the same tracers (HTO, $^{22}\text{Na}^+$, Cs^+ , and I^-) used in the clay diffusion experiments described above (Glaus et al., 2013; Tachi & Yotsuji, 2014) and we investigated their behavior in the physically and electrostatically heterogeneous flow-through chamber. The simulations were run by applying a constant flux boundary at the inlet, where the tracer solution containing HTO, $^{22}\text{Na}^+$, Cs^+ , and I^- was injected from a line source (1 cm) located at the center of the inlet boundary. Table 2 summarizes the geometry, hydraulic, transport, and surface properties used in the laboratory and field scale simulations presented in sections 4.1 and 4.2.

Figure 5 shows hydraulic conductivities, computed streamlines and spatial distribution of flow velocity in the heterogeneous domain. Due to the low hydraulic conductivity in the clay inclusion ($K_{\text{lens}}/K_{\text{matrix}} = 10^{-4}$), the flow lines diverge around the clay zone, which is hydraulically less accessible and is bypassed by most groundwater flow. The computed flow velocities suggest that the average velocity in the sandy matrix is ~ 0.5 m/d, whereas it is orders of magnitude smaller in the clay lens.

We performed a series of simulations in order to analyze the effects of different clay properties, conceptualization of processes in clay's nanopore, and physicochemical heterogeneity during the transport of multi-ionic solutions. Particularly, these simulations are targeted to explore the impact of: (i) surface charge screened by diffuse layer and interlayer,

(ii) diffusion in diffuse layer/interlayer, and (iii) thickness of diffuse layer. The details of the simulation scenarios are listed in Table 3.

In all the scenarios, ~20% and ~80% of the total intergranular porosity (i.e., FW + DL) were considered to be initially occupied by the free and Donnan water, respectively. The compositions of boundary and initial solutions, and diffusion coefficients for the different species are reported in Table 4.

Figure 6 illustrates the flux-averaged breakthrough curves of different species at the outlet of the domain for all the scenarios. The charge-neutral species (HTO) exhibits very similar breakthrough curves in all scenarios (Fig. 6a). The situation is also similar for the negatively charged species (I^-) except the minor differences in breakthrough curves of Scenario 2 and variable Donnan thickness cases (Fig. 6b). Such behaviors are expected since the uncharged tracer is not affected by the Coulombic forces, and the anions are largely excluded from the diffuse layer and fully excluded from the interlayer. Therefore, the breakthrough curves of I^- do not change much due to the variation in the surface charge properties in different scenarios. In contrast, the breakthrough curves of the cations show distinct behavior in different scenarios with similar arrival time but differences in the tailings (Fig. 6c-d). In Scenario 1, which represents the complete screening of *CEC* by diffuse layer, it is evident that diffusion in Donnan water leads to an enrichment of cationic tracers ($^{22}\text{Na}^+$, Cs^+) in the diffuse layer as reflected in the lower concentrations in the tailings of breakthrough curves of scenarios 1B and 1B' compared to scenario 1A (red lines, Fig. 6c-d).

In Scenario 2 the total *CEC* is screened by the interlayer species, and the diffuse layer is absent (Table 3). The interlayer type exchange processes appear to produce similar breakthrough curves compared to Scenario 1 where the diffuse layer was considered (blue lines, Fig. 6c-d). However, upon considering diffusion in the interlayer water (Scenario 2B), the temporal concentration profiles deviate compared to the analogous scenario (Scenario 1B). Such behavior, particularly significant for the species with the highest selectivity coefficient (Cs^+), stems from the fundamental differences between the ion-exchange like mechanisms in the interlayer and the electrostatic mechanisms in the diffuse layer.

In Scenario 3, we consider that the total surface charge (*CEC*) of the inclusion is partitioned between diffuse layer (40%) and interlayer (60%). When diffusion in the Donnan and interlayer porosity is ignored (Scenario 3A), the cationic breakthrough curves (solid green lines, Fig. 6c-d) in this case are either almost identical to the ones of the corresponding scenario containing only Donnan water (Scenario 1A) or close to the ones of the case considering only interlayer water (Scenario 2A). Scenario 3B allows diffusion of Donnan species (green dash-dotted lines), and appears to produce breakthrough curves consistent to Scenario 1B but with slightly higher concentrations at late times due to a relatively weaker enrichment of cations in the DL because only 40% of the surface charge is available to electrostatically couple the counter ions. Interestingly, allowing diffusion in the interlayer (but not in the DL, Scenario 3C) leads to significantly different breakthrough curve for Cs^+ compared to Scenario 3A but there is little effect for $^{22}\text{Na}^+$ (light green dotted lines). This can be explained from the fact that Cs^+ has 100-fold higher affinity to replace Na^+ from the interlayer space ($K_{i/\text{Na}}$, Table 2), whereas the selectivity coefficient for $^{22}\text{Na}^+$ and Na^+ is identical in this example. Finally, Scenario 3D accounts for the diffusion in all the sub-continua of the clay inclusion and it leads to the breakthrough curve that is similar to ones of scenario 3B and 3C for $^{22}\text{Na}^+$ and Cs^+ , respectively (green dashed lines). For the scenarios considering variable diffuse layer thickness (Scenario 1B' and 3D'), the cationic breakthrough curves exhibit minor differences compared to their analogous cases with constant Donnan thickness. In contrast, the influence of Donnan diffusion on the anionic breakthrough curves

in these scenarios appears to be enhanced compared to the respective constant Donnan thickness scenarios (Fig. 6b). This behavior is clearly due to the gradual contraction of the diffuse layer once the mass-transfer into the clay lens occurs, causing an increase of the ionic strength (Eq. 26).

Fig. 7 shows the two-dimensional distribution of total fluxes for the transported species in free, diffuse layer, and interlayer porosity after 8 days of simulation for Scenario 3D. Upon injection in the central portion of the inlet boundary, these solute species travel through the 2-D domain along the streamlines (Fig. 5), which diverge around the clay inclusion because of the hydraulic heterogeneity. Consequently, mass-transfer through the sandy-clayey interface is largely controlled by the diffusive/dispersive transport. The maps of the total Nernst-Planck fluxes in the free porosity confirm this behavior by showing higher magnitudes around the clay zone and almost negligible values within the inclusion (left column, Fig. 7). However, the fluxes through the diffuse layer water of the clay lens (central column, Fig. 7) are significantly higher than the free water fluxes at the same zone and their magnitude is comparable to the values in the sandy sediments surrounding the lens. Iodide shows smaller magnitude of fluxes in the DL than the cationic tracers due to its partial exclusion from the Donnan space caused by the electrostatic repulsion from the surface charge (Fig. 7e,h,k). In the interlayer water, only the fluxes for the cations exist because charge-neutral species and the anions are excluded from the interlayer (right column, Fig. 7). In both DL and IL porosities $^{22}\text{Na}^+$ and Cs^+ show similar distributions but opposite pattern with $^{22}\text{Na}^+$ flux being relatively higher in the DL and vice versa in the interlayer (Fig. 7h-i,k-l). In contrast, the background cation, Na^+ , has a negative contribution in the interlayer space reflecting the release from the surface due to the exchange with the injected tracer cations (Fig. 7o).

Mapping the different components of ionic fluxes in the heterogeneous flow-through domain helps understanding and visualizing the coupling between different charged species and allows performing a closer inspection of electrostatic effects driven by the surface and ions' charge. According to Eq. (3) and Eq. (14), these flux components in different porosities can be written as:

$$J_{i,Tot}^{\zeta} = J_{i,Disp}^{\zeta} + J_{i,Act}^{\zeta} + J_{i,Mig}^{\zeta} \quad (30)$$

As an example, we plot the maps of the different flux components for Cs^+ through all the porosities (Fig. 8). The panels in the left column illustrate the flux components in the free porewater and show a positive contribution of the electromigration flux to the displacement of Cs^+ . This is due to the Coulombic interactions coupling the diffusive/dispersive fluxes of the positively and negatively charged species to maintain the net charge balance. In fact, the electrical potential induced by the variation in ionic mobility leads to an acceleration of Na^+ ($D_{aq} = 1.33 \times 10^{-9} \text{ m}^2/\text{s}$) and deceleration of Cl^- ($D_{aq} = 2.03 \times 10^{-9} \text{ m}^2/\text{s}$) among the species present at higher concentration (Table 4). As a consequence, the tracer ions present in smaller concentrations are electrostatically pulled by the sodium and chloride ions leading to an enhanced displacement of all tracer cations (including Cs^+) and vice versa for the tracer anions. Such behavior was also observed in the previous study involving pH fronts propagation (Muniruzzaman & Rolle, 2015) and cannot be explained from a Fickian solute transport model. The situation is opposite in the Donnan and interlayer porosities, where the negative contribution of J_{Mig} leads to the reduced diffusive movement of Cs^+ through these fractions of the porosity (Fig. 8h,i). It is remarkable that the magnitudes of J_{Mig} is in the same order as the diffusive/dispersive fluxes in the free water (J_{Disp}) demonstrating the strong influence of electrostatic cross-coupling in these porosities. Indeed, J_{Mig} and J_{Disp} counterbalance to yield a total flux (J_{Tot}) that is very close to zero in certain parts of the clay inclusion (Fig. 8b-c). The activity gradient fluxes are negligible in all domains for Cs^+ in this

particular case (Fig. 8j-l) but the species with higher concentration (Na^+ , Cl^-) show relatively higher magnitude that are comparable to the electromigration fluxes (results not shown).

4.2 Transport in a field-scale heterogeneous sandy-clayey domain

To investigate the charge effects at larger scales, simulations were also performed in a field-scale heterogeneous sandy-clayey domain with dimensions of $20 \text{ m} \times 2 \text{ m}$ ($L \times H$). We consider a 2-D stochastically generated hydraulic conductivity field, which can be considered representative of a vertical cross-section of a heterogeneous sandy aquifer with multiple clay inclusions. The random field was generated using a Gaussian covariance model with the parameters listed in Table 2 (third column), and the irregularly shaped low-conductivity clay lenses in the binary field were created by setting a cutoff value for the hydraulic conductivity (i.e., $K_{\text{cutoff}} = 0.38 K_{\text{mean}}$) (e.g., Dykaar & Kitanidis, 1992; Werth et al., 2006; Chiogna et al., 2011). The hydraulic gradient was adjusted (3.9×10^{-3}) to produce an average flow-velocity similar to the case of the lab-scale scenarios ($\sim 0.5 \text{ m/d}$). All the hydraulic, transport, and geochemical parameters used in the simulation are reported in Table 2.

Fig. 9a illustrates a complex pattern of the streamlines that diverge around the low-conductivity clay inclusions (K ratio = 10^{-5}). The seepage velocity is also spatially variable and it is highest where the groundwater flow is focused in the permeable sandy matrix and lowest in the impermeable clay zones (Fig. 9b). The distribution of the surface charge indicates zero charge in the sandy matrix and negative values in the inclusions (Fig. 9c).

Transport simulations were performed considering an analogous multitracer ionic transport problem as in the laboratory scale scenario (Section 4.1): a tracer solution containing HTO, $^{22}\text{Na}^+$, Cs^+ , and I^- was injected from a line source (25 cm) located at the center of the inlet boundary of the flow-through domain, as indicated by the red lines in Fig. 9 (d, g, j, m). However, in these simulations a pulse injection with duration of 2 days was considered. For simplicity, we only selected the case analogous to Scenario 3D at the laboratory scale (Table 3), where 40% of the CEC was assigned to the DL and the remaining 60% was allocated in the interlayer. We also applied the same initial and boundary solutions as used in the lab-scale simulations (Table 4). Fig. 9d-o show the results of the transport simulations in the 2-D field-scale domain. The effects of physical and electrostatic heterogeneity are clearly evident in the irregular shape of the solute plumes in the free porosity. The impact of diffusion and charge effects is also visible in this large-scale transport simulations as indicated by the distinct plume shapes for different species in free water. Due to the electrostatic attraction in DL, cations are enriched and I^- is depleted in the DL (Fig. 9h,k,n). HTO travels similarly both in the DL and free porosity because it is not affected by the surface charge (Fig. 9e). In the interlayer water, HTO and I^- are excluded and the cationic concentrations show a similar pattern as in the DL sub-continuum, except that the magnitude of interlayer concentrations is orders of magnitude higher (Fig. 9l,o).

We also analyze the depth-integrated breakthrough curves of the different species at the end of the 2-D heterogeneous domain. Fig. 10 shows the results of two particular numerical tests considering: (i) only physical heterogeneity with a single-continuum and a Fickian formulation with the compound-specific diffusive/dispersive terms (red dashed lines), and (ii) both physical and electrostatic heterogeneity with the multi-continua and Nernst-Planck formulation (black solid lines). The first approach is representative of conventional, high-resolution transport simulations in a heterogeneous aquifer, whereas the second approach is a novel description that is possible with the MMIT-Clay model presented in this work. The first scenario considering only physical heterogeneity (i.e., considering heterogeneous distribution of K , ν , D_L , and D_T but ignoring the charge interactions) shows

tailings in the solute breakthrough curves (red dashed lines). Such behavior is indicative of mass-transfer limitations between the fast flow (sandy matrix) and slow flow (clay inclusions) regions. In the second scenario, which considers both physical and electrostatic heterogeneity, the temporal profile of HTO remains almost identical (Fig. 10a). The situation is also similar for I^- with smaller differences in the breakthrough peak and tailing compared to the first scenario (Fig. 10b). These outcomes are caused by the fact that the uncharged species is not affected by the surface charge and the anionic species is electrostatically repelled from the negatively charged surface within the DL and IL sub-continua. In contrast, the electrostatic heterogeneity significantly affects the breakthrough curves of the cations as reflected by the smaller peak concentrations (28% and 44% relative differences for $^{22}\text{Na}^+$ and Cs^+ , respectively) compared to the previous scenario (Fig. 10c-d). Interestingly, the breakthroughs of these cationic species do not show tailings upon considering the charge effects in this scenario (black solid lines, Fig. 10c-d). Such behavior, indicative of effective mass-exchange between free porosity and the other sub-continua, is indeed triggered by the electrostatically induced enrichment of these counter-ions in the DL and IL fractions of the porewater in clay inclusions leading to a sorption-like process. Consequently, $^{22}\text{Na}^+$ and Cs^+ are effectively retained at the negative surface within the clay zones leading to a smaller peak concentration and diminished tailings in the breakthrough curves. These results show that ignoring the mechanisms of electrostatic interaction in DL and IL considerably affects the outcomes of transport simulations in clay systems and leads to the overestimation of the cationic peak concentrations.

5 Conclusions

Subsurface flow systems comprising both sandy and clayey porous media entail a spatially variable distribution of both physical (e.g., hydraulic conductivity) and electrostatic properties (e.g., surface charge). The displacement of charged species in these systems is affected not only by the classic advection and dispersion processes but also by solute/solute and solute/surface charge interactions between the different species. Therefore, mechanistic reactive transport models are instrumental for the fundamental understanding of solute and contaminant displacement occurring in natural and engineered systems involving clay sediments and coupled charge displacement in the pore water of clayey and sandy porous media. In this study, we have presented a multicomponent reactive transport approach capable of taking into account the electrostatic effects induced by surface/ions charge and a wide range of chemical reactions in 1-D and 2-D homogeneous and heterogeneous flow-through porous media. The key features of the proposed modeling approach include: (i) formulation of different sub-continua to consider diffuse layer (based on Donnan approximation) and interlayer processes; (ii) calculation of the ionic fluxes based on Nernst-Planck equations in each sub-continuum, and the transport of all aqueous species instead of only the chemical components; (iii) compound-specific and spatially-variable description of local hydrodynamic dispersion in free porosity, and pore-diffusion in Donnan and interlayer porosities allowing accurate representation of pore-scale processes; (iv) capability to include activity gradient fluxes, which can be relevant in the presence of strong ionic strength variations; (v) coupling with the geochemical code PHREEQC to offer great flexibility to include a wide variety of chemical reactions. The code was validated against numerical simulations involving diffuse layer and/or interlayer calculations carried out with PHREEQC in 1-D setups, and experimental datasets obtained from diffusion cell setups in previous studies.

Numerical experiments were presented in this study to explore the impact of charge effects on multicomponent ionic transport in 2-D heterogeneous flow-through porous media, involving sandy-clayey formations at different scales. Laboratory bench-scale simulations analyzed the key importance of electrostatic interactions and highlighted the influence of different aspects such as fractions of diffuse layer vs. interlayer charge, diffuse layer thickness, and diffusion through diffuse layer/interlayer. The simulation outcomes show that both the distribution of *CEC* over DL and interlayer, as well as the diffusive movement through these sub-continua significantly impact the spatial concentration maps and breakthrough curves of the solutes. Moreover, linking the diffuse layer thickness to the ionic strength dynamically partitions the total porosity to free and Donnan porosities based on the solution compositions, thus, also produces considerably different outcomes compared to the analogous scenario with constant diffuse layer thickness. Field-scale simulations highlighted the relevance of charge effects in large scale domains. The simulation results revealed that ion-ion and ion-surface electrostatic interactions are relevant for the charged species transport not only in diffusion-dominated systems and centimeter-scale setups but also in the advection-dominated, multidimensional, and heterogeneous flow-through systems. The outcomes of the numerical experiments at both laboratory and field scales also highlight that an accurate description of the coupled transport behavior of charged species cannot be reproduced only by considering low-hydraulic conductivities at the clay layers or with a single porosity reactive transport model, but requires a multi-continua reactive transport formulation and the capability to take into account both physical and electrostatic heterogeneity in sandy-clayey media.

The model's capability of mapping diffusive/dispersive fluxes and their individual components in the different sub-continua is also an important feature elucidating the role and contribution of distinct transport mechanisms in charged porous media. Besides the investigation of charge-induced processes that was the main focus of this study, the model offers extended capability to capture a series of chemical reactions, including aqueous speciation, mineral precipitation-dissolution, degradation and kinetic reactions, mobilization of heavy metal(loid)s, acidic front propagation, and radionuclides displacement and isotope fractionation, utilizing PHREEQC as a reaction engine. Therefore, the developed MMIT-Clay framework can also be applied to subsurface systems where, besides charge interactions, other physical, chemical and biological processes are of interest (e.g., Druhan et al., 2015; Fakhreddine et al., 2016; McNeece and Hesse, 2017; Molins et al., 2012; Prigiobbe & Bryant, 2014; Poonosamy et al. 2016; Stolze et al., 2019a,b). The multidimensional and flow-through perspective on multicomponent ionic transport in heterogeneous clayey formations introduced in this study could also be extended to fully 3-D setups where complex anisotropy and flow topology may play a major role (e.g., Chiogna et al., 2014; Cirpka et al., 2015; Ye et al., 2015b-c). Further developments are also envisioned for engineering application in which the proposed model can be extended to systems involving external electrical gradients and electrokinetic transport and/or distribution of amendments in the subsurface (e.g., Reddy & Cameselle, 2009; Appelo, 2017; Martens et al., 2018; Alizadeh et al., 2019; Sprocati et al., 2019).

Acknowledgments, Samples, and Data

The datasets obtained from the simulations performed in benchmark problems (Dataset S1) as well as numerical experiments (Dataset S2) are available at Mendeley Data repository (<http://dx.doi.org/10.17632/cnry2b7w4p.1>) and are also provided in the Supporting

Information. The latter also provides a figure illustrating the schematic diagrams of the setups used in different benchmark problems (Figure S1), results of the Benchmark problem 1 and 3 including the input parameters (Table S1), and numerical implementation of water flow and ionic transport in the presented modeling framework (Section S1 and S2).

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Figure 1. Schematic diagram of the structure of the multicomponent reactive transport model (MMIT-Clay).

Figure 2. Results of Benchmark 2 showing a comparison between the MMIT-Clay simulations (lines) and experimental (markers) temporal (a-d) and spatial (e-h) profiles of HTO (a, e), I^- (b, f), $^{22}Na^+$ (c, g), and Cs^+ (d, h) in a montmorillonite plug equilibrated with a 0.1 M NaCl solution (experimental data from Tachi and Yotsuji, 2014).

Figure 3. Results of Benchmark 4: verification of the interlayer diffusion calculation against experimental data, from Glaus et al. (2013), obtained under a salinity gradient in a 5 mm (a, c) and a 10 mm (b, d) montmorillonite clay plugs. The dashed lines represent the Na^+ concentrations in the reservoirs.

Figure 4. Results for Benchmark problem 5 showing the breakthrough curves (a), and spatial profiles of the porewater compositions in the free porosity (b), Donnan porosity (c), and exchangeable surface sites (d) after 300 days.

Figure 5. Simulated streamlines and hydraulic conductivities (a); and flow velocity distribution (b) in the lab-scale domain. The flow direction is from left to right.

Figure 6. Flux-averaged breakthrough curves of HTO (a), I^- (b), $^{22}Na^+$ (c), and Cs^+ (d) at the outlet of the 2-D heterogeneous lab-scale domain.

Figure 7. Maps of the total Nernst-Planck fluxes of different species in different sub-continua for the transport in the heterogeneous, lab-scale domain (Scenario 3D, $t = 8$ days).

Figure 8. Maps of different flux components of Cs^+ through different porosities after 8 days for the transport in lab-scale domain (Scenario 3D): Total fluxes (a-c), Diffusive/dispersive fluxes (d-f), Electromigration fluxes (g-i), and Activity gradient fluxes (j-l).

Figure 9. Computed streamlines and logarithms of hydraulic conductivities (a); flow velocity distribution (b); surface charge (c); and concentration maps in free (d, g, j, m), diffuse layer (e, h, k, n), and interlayer (f, i, l, o) porewater after 25 days. Flow direction is from left to right and the red lines represent the location of the multitracer injection (d, g, j, m).

Figure 10. Depth-integrated breakthrough curves of HTO (a), I^- (b), $^{22}Na^+$ (c), and Cs^+ (d) at the outlet of the heterogeneous field-scale domain. Solid lines represent the fully Nernst-Planck solution with multi-continua transport, whereas the dashed lines represent the results from simulation using single continuum transport considering Fickian diffusion and neglecting charge interactions in the pore water and at the solid/solution interface.

Table 1. Input parameters for the simulations of benchmark problem 2, 4, and 5.

Parameters	Benchmark Problems		
	2 ^a	4 ^b	5 ^c
Length (L) [cm]	1	0.5;1 ^f	5
Discretization, Δx [mm]	1	0.50	2
Bulk density [kg/L]	0.80	1.90	1.4
Total porosity, θ [-]	0.72	0.30	0.476
Free water fraction, f_{FW} [-]	0.50	0.05	0.15
Free water tortuosity, τ_{FW} [-]	10;100;20;12.5 ^e	4;6.67 ^f	1
Donnan water tortuosity, τ_{DL} [-]	10;100;20;12.5 ^e	-	-
Interlayer tortuosity, τ_{IL} [-]	-	100	-
CEC [eq/kg]	1	0.80	0.74
Specific surface area, [m ² /g]	750	750	788
$\log K^{22}_{Na/Na}$	0	0.15	-
$\log K_{Cs/Na}$	2.4 ^d	-	-

^aAccording to the through-diffusion experiment of Tachi and Yotsuji (2004)^bAccording to the diffusion experiment of Glaus et al. (2013)^cAccording to the benchmark problem of Alt-Epping et al. (2015)^eThe value refers to the constant Donnan thickness case, whereas it dynamically changes in the variable thickness case^fTortuosity adjusted for each species (τ for HTO=10, I=100, ²²Na⁺=20, Cs⁺=12.5), and a 2-fold smaller $D_{aq,i}$ was considered in the DL^dFirst and second value refer to the experiment with 5 and 100 mm plug connected to 250 and 100 mL reservoirs, respectively**Table 2.** Summary of geometry, flow, transport, and surface parameters for the simulations in heterogeneous laboratory and field scale domains.

Parameters	Lab-Scale	Field-Scale
Domain size ($L \times H$) [m]	0.80×0.12	20×2
Discretization, $\Delta x / \Delta z$ [cm]	1/0.10	40/2
Hydraulic conductivity, sandy matrix [m/s]	1.27×10^{-2}	6.14×10^{-4}
Hydraulic conductivity, clay lenses [m/s]	1.27×10^{-6}	6.14×10^{-9}
$\sigma^2_{\ln K}$	-	1
Correlation lengths, l_x / l_z	-	2/0.10
Average flow velocity [m/d]	0.50	0.50
Total porosity, sandy matrix [-]	0.41	0.41
Total porosity, clay lenses [-]	0.72	0.72
Tortuosity, sandy matrix [-]	2.44	2.44
Tortuosity, clay lenses [-]	6.25;100 ^a	6.25;100 ^a
Source thickness at inlet boundary [cm]	1	25
Injection duration [d]	continuous	2
Cation exchange capacity, CEC [eq/kg]	0.11	0.11
Specific surface area, A_s [m ² /g]	37	37
Selectivity coefficients, $\log K_{i/Na}$	0;2 ^b	0;2 ^b

^aThe first value refers to the tortuosity in free and Donnan water, and the second value is the tortuosity in interlayer water.^bThe first and second values refer to the exchange coefficients of ²²Na⁺ and Cs⁺ for Na⁺ respectively (Eq. 10-11).

Table 3. Description of the simulation scenarios in the lab-scale domain.

Scenarios	CEC distribution	Diffusion in diffuse layer	Diffusion in interlayer	Thickness of diffuse layer ^a
1A	Total CEC in DDL	No	-	constant
1B	Total CEC in DDL	Yes	-	constant
1B'	Total CEC in DDL	Yes	-	variable
2A	Total CEC in Interlayer	-	No	-
2B	Total CEC in Interlayer	-	Yes	-
3A	40% CEC in DDL, 60% CEC in Interlayer	No	No	constant
3B	40% CEC in DDL, 60% CEC in Interlayer	Yes	No	constant
3C	40% CEC in DDL, 60% CEC in Interlayer	No	Yes	constant
3D	40% CEC in DDL, 60% CEC in Interlayer	Yes	Yes	constant
3D'	40% CEC in DDL, 60% CEC in Interlayer	Yes	Yes	variable

^aAn initial thickness of 1 nm was used which corresponds to $f^{DL} = 0.80$ as initial condition.

Table 4. Compositions of inflow and initial solutions in lab-scale simulations.

Species	Inflow (mol/L)	Initial (mol/L)	Diffusion coefficient, $D_{aq,i}$ (m ² /s)
pH	7	7	9.31×10^{-9}
HTO	10^{-3}	0	2.24×10^{-9}
²² Na ⁺	10^{-3}	0	1.33×10^{-9}
Cs ⁺	10^{-3}	0	2.07×10^{-9}
I ⁻	10^{-3}	0	2.00×10^{-9}
Na ⁺	0.239	10^{-4}	1.33×10^{-9}
Cl ⁻	0.24	10^{-4}	2.03×10^{-9}