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Impact of diffuse layer processes on contaminant forward and back diffusion in heterogeneous sandy-clayey domains

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ABSTRACT

Low-permeability aquitards can significantly affect the transport, distribution, and persistence of contaminant plumes in subsurface systems. Although such low-permeability materials are often charged, the key role of charge-induced electrostatic processes during contaminant transport has not been extensively studied. This work presents a detailed investigation exploring the coupled effects of heterogeneous distribution of physical, chemical and electrostatic properties on reactive contaminant transport in field-scale groundwater systems including spatially distributed clay zones. We performed an extensive series of numerical experiments in three distinct heterogeneous sandy-clayey domains with different levels of complexity. The flow and reactive transport simulations were performed by explicitly resolving the complex velocity fields, the small-scale electrostatic processes, the compound-specific diffusive/dispersive fluxes and the chemical processes utilizing a multi-continua based reactive transport core (MMiT-Clay). In each particular domain, numerical experiments were performed focusing on both the forward and back diffusion through the sandy-clayey interfaces. The results illuminate the control of microscopic electrostatic mechanisms on macroscopic mass transfer. Coulombic interactions in the clay’s diffuse layer can significantly accelerate or retard a particular species depending on its charge. Furthermore, the chemical heterogeneity plays a major role in mass storage and release during reactive transport. Neglecting such processes can lead to substantial over- or underestimation of the overall transport behavior, which underlines the need for integrated physical, chemical and electrostatic approaches to accurately describe mass transfer processes in systems including low-permeability inclusions.

Keywords: clay, Donnan equilibrium, low permeability porous media, heterogeneity, back diffusion, reactive transport modeling
1. INTRODUCTION

The occurrence of low-permeability media is common in many natural subsurface systems. They can act as aquitards and play a key role on the fate and transport of contaminants in groundwater flow systems (e.g., Cherry et al., 2004; Liu et al., 2004; Chapman and Parker, 2005; Zhan et al., 2009; Marble et al., 2010; Seyedabbasi et al., 2012; Adamson et al., 2016; Yang et al., 2017; Muskus and Falta, 2018). Due to the low hydraulic conductivity, advective flow is typically slow in such media, making them rather inaccessible for the groundwater flow. Therefore, mass transport in these low-permeability zones is known to be mainly controlled by diffusive mechanisms (e.g., Gillham et al., 1984; Mackay and Cherry, 1989; Harrison et al., 1992; Haggerty and Gorelick, 1995; Ball et al., 1997; Gusawa and Freyberg, 2000; LaBolle and Fogg, 2001; Parker et al. 2004; 2008; Rasa et al., 2011; Rezaei et al., 2013; Yang et al., 2014; Parker and Kim, 2015; Falta and Wang., 2017; Lari et al., 2019). Thus, the presence of such low permeability regions within or at the boundary of a permeable aquifer can significantly enhance the persistence of contaminant plumes because the low-conductive regions can act as effective traps for the contaminants. In heterogeneous groundwater systems, diffusive mass-transfer from high- to low-permeability zones can lead to the storage of substantial contaminant mass in clay regions (typically known as “forward” or “inward” diffusion) (e.g., Liu and Ball, 2002; Chapman and Parker, 2005; Parker et al., 2008; Sale et al., 2008; Seyedabbasi et al., 2012; Yang et al., 2014; 2016; Manaka and Takeda, 2016). The stored contaminant mass in the low-permeability zones can serve as a long-term secondary contaminant source and can be persistently released again in the high-permeability regions upon flushing of the latter and reversal of the concentration gradients. This process is usually known as “back” or “reverse” diffusion (e.g., Ball et al., 1997; Harvey and Gorelick, 2000; Parker et al., 2004; Rasa et al., 2011; Chapman et al., 2012; Rezaei et al., 2013; Parker and Kim, 2015; Tatti et al., 2016; 2019; Yang et al., 2015; 2017). Another important feature of naturally
occurring low-permeability materials, such as clays, clay rocks or shales, is the presence of charged mineral surfaces, which also exert a key control on the transport, distribution and remediation of the charged contaminants (e.g., radionuclides, toxic metals/metalloids, or even ionized organic compounds such as some perfluorinated alkylated substances) as well as major groundwater ions (e.g., Birgersson and Karnland, 2009; Gimmi and Kosakowski, 2011; Glaus et al., 2013; Jougnot et al., 2009; Tertre et al., 2018; Tinnacher et al., 2016). The surface charge induces electrostatic interactions at the solid-liquid interface, and leads to the formation of the so called “diffuse layer (DL)” where the counter-ions are attracted and the co-ions are repelled (e.g., Descostes et al., 2008; Tournassat and Appelo, 2011; Van Loon et al., 2007; Wersin et al., 2017; 2018; Wigger and Van Loon, 2017). Consequently, the porewater in such charged low-permeability media is composed of two distinct regions: a diffuse layer, which is located directly at the proximity of the surface and counterbalances the surface charge, and a “free” or “bulk” water region, which is located farther from the surface and contains a charge-balanced solution composition (e.g., Sposito, 1992; Appelo and Wersin, 2007; Charlet et al., 2017; Tournassat and Steefel, 2015; Appelo et al., 2008; Soler et al., 2019; Tournassat and Appelo, 2011). In addition to the surface-driven electrostatic processes, species-species interactions, due to the Coulombic effects caused by ions’ charge, can also significantly affect the mass flux and displacement of the charged contaminants in a multi-ionic environment, which is a typical scenario in groundwater chemistry (e.g., Boudreau et al., 2004; Cussler, 2009). In fact, the impact of such Coulombic interactions was shown to be significant not only in diffusion-dominated systems or under laboratory conditions (e.g., Appelo and Wersin, 2007; Felmy and Weare, 1991; Giambalvo et al., 2002; Liu et al., 2011) but also under advection-dominated flow regimes and/or at field-scales (e.g., Appelo et al., 2008; 2010; Rolle et al., 2013; Muniruzzaman et al., 2014; Muniruzzaman and Rolle, 2015; 2017). Furthermore, groundwater flow systems comprising both high- and low-permeability materials may also entail inhomogeneous
distribution of chemical properties, which can further influence degradation, retardation, and chemical transformation of subsurface solute plumes (e.g., Marble et al., 2010; Rasa et al., 2011; Yang et al., 2016; Muskus and Falta, 2018; Lari et al., 2019; Muniruzzaman and Pedretti, 2020). Therefore, the description of solute transport processes in heterogeneous systems comprising low-permeability regions requires the explicit treatment of these spatially distributed physicochemical and electrostatic processes within a rigorous reactive transport modeling framework.

Although physical mass-transfer processes are well studied in the context of forward and back diffusion of contaminant plumes (e.g., Liu and Ball, 2002; Casaya et al., 2000; Sale et al., 2008; Parker et al., 2008; Chapman et al., 2012; Yang et al., 2014; 2017; Adamson et al., 2016; Falta and Wang, 2017; Tatti et al., 2018), the electrostatic and chemical mechanisms are rather unexplored in the subsurface and contaminant hydrology literature and their impacts on reactive transport in complex groundwater aquifer-aquitard systems are not yet understood. In fact, only a few contributions have considered simultaneous effects of the heterogeneous distribution of physical and chemical properties during subsurface solute transport but without specifically focusing on low-permeability media (e.g., Yang and Samper, 2009; Samper and Yang, 2006; Muniruzzaman and Rolle, 2016; Soltanian et al., 2015; 2018). Moreover, charge-induced diffuse layer processes have seldom been studied in connection with subsurface reactive transport in complex heterogeneous flow-through systems, even though the relevance of such processes on diffusive mass transport is increasingly recognized in the geochemical literature (e.g., Leroy et al., 2006; Muurinen et al., 2004; Tournassat and Appelo, 2011; Glaus et al., 2007; 2013; Tachi and Yotsuji, 2014; Tertre et al., 2015; Tournassat and Steefel, 2019). In this study, we present a thorough investigation exploring the coupled effects of heterogeneous distributions of physical, chemical and electrostatic properties in the context of reactive contaminant transport in field-scale groundwater systems including low-
permeability porous media. We performed an extensive series of numerical experiments in three distinct heterogeneous sandy-clayey two-dimensional domains with different levels of complexity. The reactive transport simulations were performed by considering the small-scale charge interactions at surface/solution interfaces and within the pore water, the compound-specific diffusive/dispersive fluxes and their electrostatic coupling, and the chemical reactive processes utilizing a recently published multi-continua based multicomponent reactive transport code, MMIT-Clay (Muniruzzaman and Rolle, 2019). In each particular domain, numerical experiments were performed focusing on both forward and back diffusion through the sandy-clayey interfaces and by considering sequential levels of heterogeneity with respect to the different properties relevant in the governing physical, electrostatic and chemical mechanisms. The results were analyzed in terms of solute breakthrough curves at the domains’ outflow boundary, spatial concentration distributions of tracer plumes, computed Nernst-Planck fluxes of transported ionic solutes in the individual sub-continua (free water and diffuse layer), and stored (and released) masses of the different solutes in (from) the clay inclusions during mass exchange between low- and high-permeability zones.

2. Modeling Approach

2.1 Theoretical background

In charged porous media, such as clay, the concentrations in the diffuse layer (DL) and the free water (FW) are typically described by the Donnan equilibrium (e.g., Donnan and Guggenheim, 1932; Appelo et al., 2008; 2010; Gimmi and Alt-Epping, 2018):

\[ c_{i,DL}^{FW} = \Gamma_i c_{i,FW} \exp \left( \frac{-z_i F \Phi_{DL}}{RT} \right) \]  

(1)
where \( c_{i}^{DL} \) and \( c_{i}^{FW} \) [mol/L] are the concentrations in the diffuse layer and free water porosities, respectively, \( \Gamma_{i} [-] \) represents the ratio of the activity coefficients in the free and Donnan water (\( = \gamma_{i}^{FW} / \gamma_{i}^{DL} \)), \( z_{i} [-] \) is the charge number of species \( i \), \( \phi^{DL} [V] \) is the mean electrostatic potential in the diffuse layer water, \( F [J/V/eq] \) is Faraday’s constant, \( R [J/mol/K] \) is the ideal gas constant, and \( T [K] \) is the temperature. The net charge in the diffuse layer water is compensated by the total charge of the mineral surfaces, and can be expressed by the so called Donnan polynomial (e.g., Gimmi and Alt-Epping, 2018; Appelo, 2017): 

\[
V_{DL} \sum_{i=1}^{N} z_{i} c_{i}^{DL} + Su = 0
\]  

where, \( V_{DL} [L] \) is the volume of diffuse layer water, and \( Su [mol] \) is total surface charge.

The diffusive movement of dissolved solutes in both the free water and the diffuse layer domains is described by the Nernst-Planck equations (e.g., Appelo and Wersin, 2007; Boudreau et al., 2004):

\[
J_{i}^{FW} = -D_{aq,i}^{FW} \left( \nabla c_{i}^{FW} + c_{i}^{FW} \nabla \ln \gamma_{i}^{FW} + \frac{z_{i} F}{RT} c_{i}^{FW} \nabla \phi_{d}^{FW} \right)
\]  

\[
J_{i}^{DL} = -D_{aq,i}^{DL} \left( \nabla c_{i}^{DL} + c_{i}^{DL} \nabla \ln \gamma_{i}^{DL} + \frac{z_{i} F}{RT} c_{i}^{DL} \nabla \phi_{d}^{DL} \right)
\]
electrical current \( (I \equiv \sum_{i=1}^{N} z_i J_i = 0) \), therefore, the electrical gradient terms in the above equations can be expressed as:

\[
\nabla \varphi_a^\zeta = - \sum_{i=1}^{N} \left[ z_i D_{aq,i}^\zeta \left( 1 + \frac{\partial \ln \gamma_i^\zeta}{\partial \ln c_i^\zeta} \right) \nabla c_i^\zeta \right] \tag{5}
\]

where, the subscript \( \zeta \) (= FW or DL) indicates the respective parameters in a particular domain of interest (i.e., free water or diffuse layer porosity). In the following we consistently use \( \zeta \) as an index for the free water and diffuse layer porosities and to represent the analogous equations for both of these domains.

After substituting Eq. (5) into Eqs. (3) and (4), the Nernst-Planck equation in both sub-continua takes the form:

\[
J_i^\zeta = -D_i^\zeta \left( 1 + \frac{\partial \ln \gamma_i^\zeta}{\partial \ln c_i^\zeta} \right) \nabla c_i^\zeta + \frac{D_i^\zeta}{\sum_{j=1}^{N} (z_j^2 D_{aq,j}^\zeta c_j^\zeta)} \sum_{j=1}^{N} \left[ z_j D_{aq,j}^\zeta \left( 1 + \frac{\partial \ln \gamma_j^\zeta}{\partial \ln c_j^\zeta} \right) \nabla c_j^\zeta \right]. \tag{6}
\]

Compared to the common Fick’s law, this formulation provides a more rigorous description of the diffusive movement of charged species because it explicitly considers the movement of a particular species not only due to its own mobility and concentration gradient but also due to the coupling with the concentrations, mobilities, and activity coefficient gradients of all other ions in the system. Such species-species coupling can significantly modify the diffusive fluxes of charged species to maintain local electroneutrality (e.g., Boudreau et al., 2004). The importance of these Coulombic effects has been demonstrated in the literature both in diffusion and advection dominated systems at laboratory and field scales (e.g., Ben-Yaakov, 1972; Felmy and Weare, 1996; Giambalvo et al., 2002; Appelo and Wersin, 2007; Appelo et al., 2008; 2010; Liu et al., 2011; Rolle et al., 2013; 2018, Muniruzzaman et al., 2014; Muniruzzaman and Rolle, 2015; 2017).
The above equation can be further rearranged to a more compact notation as:

$$J^\xi_i = -\sum_{j=1}^{N} D^\xi_{ij} \left( 1 + \frac{\partial \ln \gamma_j}{\partial \ln c_j^\xi} \right) \nabla c_j^\xi$$  \hspace{1cm} (7)

where $D^\xi_{ij}$ is the matrix of inter-diffusion coefficients coupling the flux of ion $i$ and the gradient of ion $j$:

$$D^\xi_{ij} = \delta_{ij} D^\xi_i - \frac{z_i z_j D_{aq,i} \gamma_j^\xi D_{aq,j}^\xi c_i^\xi}{\sum_{j=1}^{N} (z_j^2 D_{aq,j}^\xi c_j^\xi)}$$  \hspace{1cm} (8)

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

### 2.2 Governing flow and transport equations

In this study, we consider two-dimensional heterogeneous domains under steady-state flow and transient reactive transport conditions. The governing equations for the groundwater flow in such systems can be expressed as (e.g., Cirpka et al., 1999a):

$$\nabla \cdot (K \nabla h) = 0$$  \hspace{1cm} (9)

$$\nabla \cdot (K^{-1} \nabla \psi) = 0$$  \hspace{1cm} (10)

where, $h$ [m] is the hydraulic head, $\psi$ [m$^2$/s] is the stream function, and $K$ [m/s] is the tensor for hydraulic conductivity. In heterogeneous domains, the solution of the flow equation is an essential step to obtain the distribution of the flow velocity field, which is necessary to solve multicomponent reactive transport problems.

By explicitly considering the electrostatic effects and the diffuse layer processes occurring in charged porous media, as described in the previous section, the mass balance equation for the multi-continua based multicomponent reactive transport can be written as:
\[
\begin{align*}
\theta \left[ \frac{\partial}{\partial t} (f^{FW} c_i^{FW}) + \frac{\partial}{\partial t} (f^{DL} c_i^{DL}) \right] &= -q \cdot \nabla c_i^{FW} + \nabla \cdot \left[ \theta \sum_{j=1}^{N} f^{FW} D_{ij}^{FW} \left( 1 + \frac{\partial \ln y_j^{FW}}{\partial \ln c_j^{FW}} \right) \nabla c_j^{FW} \right] \\
&\quad + \nabla \cdot \left[ \theta \sum_{j=1}^{N} f^{DL} D_{ij}^{DL} \left( 1 + \frac{\partial \ln y_j^{DL}}{\partial \ln c_j^{DL}} \right) \nabla c_j^{DL} \right] - \sum_{r=1}^{N_r} \nu_r R_r
\end{align*}
\] (11)

where \( \theta \) [-] is the total porosity, \( f^{FW}, f^{DL} \) [-] represent the fractions of the total porosity occupied by the free water and diffuse layer respectively \( (f^{FW} + f^{DL} = 1) \), \( t \) [s] is time, \( q \) [m/s] is the specific discharge vector in the free porosity, \( R_r \) [mol/m\(^2\)/s] is the reactive source/sink term, \( \nu_{ir} \) [-] is the stoichiometric coefficient of species \( i \) for \( r \)-th reaction, and \( D_{ij}^{FW}, D_{ij}^{DL} \) [m\(^2\)/s] are the tensors for the cross-coupled dispersive terms (e.g., Muniruzzaman et al., 2014; Muniruzzaman and Rolle, 2016), which are formally analogous to the inter-diffusion coefficients in Eq. (8) but expressed with the local hydrodynamic dispersion coefficients in a two-dimensional local coordinate system, oriented along the principal flow directions, the entries of these cross-coupled dispersion tensor in the respective porosity domains can be expressed as (e.g., Muniruzzaman and Rolle, 2019):

\[
D_{ij}^{\xi} = \begin{bmatrix}
\delta_{ij} D_{L,i}^{\xi} - \frac{z_i z_j D_{L,i}^{\xi} D_{L,j}^{\xi}}{\sum_{j=1}^{N} (z_j^2 D_{L,j}^{\xi} c_j)} & 0 \\
0 & \delta_{ij} D_{T,i}^{\xi} - \frac{z_i z_j D_{T,i}^{\xi} D_{T,j}^{\xi}}{\sum_{j=1}^{N} (z_j^2 D_{T,j}^{\xi} c_j)}
\end{bmatrix}
\] (12)

where \( D_{L,i}^{\xi} \) and \( D_{T,i}^{\xi} \) [m\(^2\)/s] are the longitudinal and transverse components of the hydrodynamic self-dispersion coefficients (i.e., when a particular charged species is transported independently, i.e., “liberated state”, from the other ions in a multicomponent solute environment) in the corresponding domains. Such local hydrodynamic dispersion coefficients are essential for an accurate representation of diffusive/dispersive transport. In this study we used the following parameterizations involving a linear relation for the longitudinal component (Guedes de Carvalho
and Delgado, 2005; Kurotori et al., 2019), and a non-linear compound-specific relation for the transverse component (Chiogna et al., 2010; Rolle et al., 2012) in the free water porosity:

\[
D_{FW}^{L,j} = D_{FW}^{P,j} + 0.5v_d \\
D_{FW}^{T,j} = D_{FW}^{P,j} + D_{aq,j}^{FW}\left(\frac{Pe_t^2}{Pe_t^2 + 4\delta^2}\right)^{\beta} 
\]

(13)

where, \(d\) [m] is the average grain size diameter, \(D_{FW}^{P,j}\) [m²/s] and \(v\) [m/s] are the pore diffusion coefficient and the seepage velocity in the free water domain, \(Pe_t\) [-] is the grain Péclet number, \(\delta\) [-] is the ratio between the length of a pore channel and its hydraulic radius, \(\beta\) [-] is an empirical exponent that accounts for the effects of incomplete mixing in the pore channels. We used values of \(\delta=5.37\) and \(\beta=0.5\), which were provided by a comprehensive analysis of transverse dispersion datasets in two-dimensional and three-dimensional setups (Ye et al., 2015a). In this study, we consider advective transport only in the free porosity, whereas the mass transport in the diffuse layer is assumed to occur by diffusive mechanisms only. The velocity-independent pore diffusion terms in each individual sub-domain can be expressed as: \(D_{P,j}^{\pm} = D_{P,j} / \tau^{\pm}\), where \(\tau^{\pm}(= \tau^{FW} \text{ or } \tau^{DL})\) [-] is the tortuosity.

In the simulations involving heterogeneous domains, a spatially variable description of the local self-dispersion coefficients is a prerequisite for accurately capturing the mass transport processes. In this study, we consider the grain size diameter in the above equation as a function of the local hydraulic conductivity by adopting the Hazen approximation: \(d \approx c\sqrt{K}\), where \(c = 0.01\) m⁰.⁵ s⁻⁰.⁵ is an empirical proportionality constant (Hazen, 1892), which was also adopted in previous studies on high-resolution transport in heterogeneous domains (e.g., Eckert et al., 2012; Rolle et al., 2013b).

This multi-continua based formulation ensures a greatly improved representation of the multicomponent ionic transport in heterogeneous charged porous media by explicitly taking into
account the electrostatic processes, inter-ionic coupling between diffusive/dispersive fluxes, concentration and activity gradients, and spatially variable description of the local hydrodynamic self-dispersion coefficients. The flow and transport equations presented above are solved with a recently developed multi-continua based reactive transport simulator, MMIT-Clay (Multidimensional Multicomponent Ionic Transport in Clay) (Muniruzzaman and Rolle, 2019). The code uses a mixed finite element method to solve the groundwater flow equations and to obtain the local velocity field. In contrast, the multicomponent ionic transport in the free water and diffuse layer porosities is solved with a finite volume method in streamline-oriented grids following the approach of Cirpka et al. (1999a,b). Furthermore, MMIT-Clay uses PHREEQC (Parkhurst and Appelo, 2013) as a reaction engine, utilizing the Phreeqc-RM module (Parkhurst and Wissmeier, 2015), to allow flexibility to include all the chemical reactions that can be handled with PHREEQC (e.g., Jara et al. 2017; Healy et al., 2018; Rolle et al. 2018; Sprocati et al. 2019; Muniruzzaman et al., 2020). Further details regarding numerical methods, implementation and solution approaches, and the verification of the code are available in Muniruzzaman and Rolle (2019).

3. PROBLEM STATEMENT
To investigate the impact of electrostatic interactions during fluid flow and conservative and reactive transport of charged solutes in low-permeability zones, we perform numerical experiments in two-dimensional heterogeneous sandy-clayey domains representing vertical transects of groundwater aquifer systems. In particular, we consider three distinct flow-fields involving clay inclusions embedded within a sandy matrix and heterogeneous distributions of physical, chemical and electrostatic properties. The simulations include solute species with different charge (i.e., positively charged, negatively charged and charge-neutral tracer species), and their transport and
mass-exchange behaviors are analyzed from the perspective of forward and back diffusion problems between the low-conductivity clay inclusions and the more permeable sandy matrix.

3.1 Heterogeneous conductivity fields

The reactive transport simulations are performed in three specific hydraulic conductivity fields involving similar dimensions but different extents of heterogeneity and permeability contrast. The first conductivity field (Setup A) is characterized by a 20 m long and 2.20 m thick domain, where a heterogeneous sandy aquifer is underlain by a 20 cm thick clay layer (Fig. 1a). The upper sandy layer is generated utilizing the hydraulic conductivity statistics reported for the mildly heterogeneous Borden aquifer \(\sigma_{lnK}^2 = 0.29\) (Sudicky, 1986) and summarized in Table 1. The clay layer is assumed to have uniform hydraulic conductivity, which is several orders of magnitude smaller compared to the sandy matrix.

The second (Setup B) and the third (Setup C) conductivity fields represent 2-D domains with dimensions of 20 m \(\times\) 2 m (L\(\times\)W) and involve relatively higher heterogeneity \(\sigma_{lnK}^2 = 1\). Unlike the single clay layer in Setup A, these two fields include multiple randomly generated clay inclusions within a sandy matrix (Fig. 1b-c). Such setups can be considered representative of vertical cross-sections of a heterogeneous sandy aquifer where several low-permeability clay zones are embedded. Both of these conductivity fields are generated using the same statistical parameters (Table 1) but their major difference is associated to the distribution of hydraulic conductivity within the sandy matrix. Setup B represents a binary field with a uniform hydraulic conductivity \(6.14 \times 10^{-4} \text{ m/s}\) for the sandy matrix (Fig. 1b), whereas we consider a random distribution of hydraulic conductivities for the sandy material in Setup C (Fig. 1c).
Fig. 1. Maps of hydraulic conductivities and computed streamlines (a-c), and distribution and orientation of the velocity field (d-f) in Setup A (a, d), B (b, e), and C (c, f): the red vertical lines (upper row) represent the inflow boundary condition. Flow direction is from left to right.

In all cases, the random conductivity field is generated using a Gaussian covariance model and by following the spectral approach of Dykaar and Kitanidis (1992). The summary of the parameters used in the generation of all corresponding fields is reported in Table 1. In order to obtain the low-conductivity inclusions in Setup B and C, we used a cut off value for the hydraulic conductivity (e.g., Werth et al., 2006; Chiogna et al., 2011). In these two particular cases, the clay inclusions were designed to occupy ~20% of the domain area (e.g., Lee et al., 2018). In the sandy matrix, the mean hydraulic conductivities for Setup A and C were 9.75×10^{-5} and 6.14×10^{-4} m/s, respectively whereas a uniform value of 6.14×10^{-4} m/s was considered, after thresholding, to obtain the binary field in Setup B. In contrast, the conductivity of the clay inclusions was set to 6.14×10^{-9} m/s for all cases. In all the simulation scenarios, the hydraulic gradient was adjusted to obtain an average flow velocity of 0.1 m/day. The flow is solved by applying no-flow boundaries at the top and bottom, and fixed hydraulic head boundaries at the left- and right-hand side of the domain. It is apparent that the heterogeneous distribution of hydraulic conductivity leads to complex patterns of the streamlines, which diverge around the clay zones (Fig. 1a-c) where flow velocity is orders of magnitude smaller in all setups (Fig. 1d-f). In contrast, the streamlines are focused in the high-
permeable sandy regions (red colors in Fig. 1) because of the higher magnitudes of the seepage velocity. The velocity distribution is also different between Setup B and C due to the spatial variability of hydraulic conductivity of the sandy matrix in Setup C.

Table 1. Geometry and hydraulic parameters used in the generation of heterogeneous flow fields.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Setup A</th>
<th>Setup B</th>
<th>Setup C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Domain size (L×W) [m]</td>
<td>20 × 2.20</td>
<td>20 × 2</td>
<td>20 × 2</td>
</tr>
<tr>
<td>Discretization, Δx/Δz [m]</td>
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<td>0.4/0.02</td>
<td>0.4/0.02</td>
</tr>
<tr>
<td>Mean hydraulic conductivity, sandy matrix [m/s]</td>
<td>9.75×10⁻³, 6.14×10⁻⁴a</td>
<td>6.14×10⁻⁴b</td>
<td></td>
</tr>
<tr>
<td>Hydraulic conductivity, clay lenses [m/s]</td>
<td>6.14×10⁻⁹, 6.14×10⁻⁹b</td>
<td>6.14×10⁻⁹b</td>
<td></td>
</tr>
<tr>
<td>Variance, sandy matrix, σ²lnK</td>
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<td>1.00b</td>
<td></td>
</tr>
<tr>
<td>Length scale parameters, lx/lz</td>
<td>0.56/0.12</td>
<td>2.0/1.0</td>
<td>2.0/1.0</td>
</tr>
<tr>
<td>Hydraulic gradient [-]</td>
<td>5.40×10⁻³, 5.80×10⁻³</td>
<td>7.80×10⁻³</td>
<td></td>
</tr>
</tbody>
</table>

*aThis setup refers to a binary field, therefore, a uniform value was allocated throughout the sandy matrix.

*bThis value refers to the variance of the original Gaussian kernel (i.e., before creating the clay lenses).

3.2 Distribution of electrostatic and chemical properties

In addition to the heterogeneous distribution of the physical property (i.e., hydraulic conductivity), we also perform simulations to analyze the effects of variability of the electrostatic and chemical properties on the multicomponent solute transport. In this study, we particularly refer to the surface charge of the solid phase as the electrostatic property, and the variation in ion-exchange reaction sites (CEC\textsuperscript{Ex}) as the chemical heterogeneity. In all the considered domains, we assume that the sandy matrix is electrostatically charge-neutral, whereas the clay inclusions contain a negatively charged surface with a value of 0.11 eq/kg, which is representative of the charge density of Opalinus clay (e.g., Appelo and Wersin, 2007; Appelo et al., 2010) (Fig. 2a-c). The same electrostatic properties were used in the different simulations since we considered the same type of clay in the different setups (Table 2). Within the clay inclusions, we assume that 20% of the total porosity is occupied by the charged balanced free water, whereas the remaining 80% is occupied by the diffuse layer. Such properties are also consistent with the values reported in the studies involving Opalinus clay (e.g., Appelo et al., 2008; 2010).
For the sake of simplicity, as chemical reactive processes we only focus on ion exchange reactions. The distribution of the chemical property within sandy material is generated by considering the ion exchange reaction sites as a function of hydraulic conductivity (Fig. 2d-f). Specifically, we use the following relationship that has been validated with field data and has also been adopted in several previous studies (e.g., Christiansen et al., 1998; Jacques et al., 1999; Yang and Samper, 2009):

\[
\ln CEC^{Ex} = a \ln K + b
\]  

where, \( CEC^{Ex} \) [mol/kg] is the cation exchange capacity for the ion exchange reactions, \( a \) and \( b \) represent the coefficients relating \( CEC^{Ex} \) with hydraulic conductivity, \( K \). Such relationship implies higher cation exchange capacities in the low-permeability regions and vice versa (Fig. 2d-f). In the simulations presented in this study, we used the value of coefficient \( a \) equal to \(-0.59\), which was obtained for a sandy aquifer in a field study performed by Christiansen et al. (1998). For the ion exchange reactions within the clay inclusions we have assumed that 10% of the clay’s total surface charge is allocated for the ion exchange reactions, whereas the remaining portion is available to the electrostatic processes in the diffuse layer (e.g., Alt-Epping et al., 2015; Appelo and Wersin, 2007; Appelo et al., 2010). Similar to the physical properties in Fig. 1, chemical properties also result in a binary distribution for Setup B and a random distribution for Setup A and C (Fig. 2d-f). Table 2
reports the mean parameters for the electrostatic, chemical and transport properties in the sandy matrix and clay inclusions, whereas their spatial variability is shown in Fig. 2.

Table 2. Transport, surface, and ion exchange parameters used in all simulations.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average flow velocity [m/d]</td>
<td>0.10</td>
</tr>
<tr>
<td>Total porosity, sandy matrix [-]</td>
<td>0.41</td>
</tr>
<tr>
<td>Total porosity, clay lenses [-]</td>
<td>0.72</td>
</tr>
<tr>
<td>Fraction of free porosity in clay, $f^{FW}$ [-]</td>
<td>0.20</td>
</tr>
<tr>
<td>Tortuosity, sandy matrix [-]</td>
<td>2.44</td>
</tr>
<tr>
<td>Tortuosity, clay lenses [-]</td>
<td>6.25</td>
</tr>
<tr>
<td>Injection type</td>
<td>continuous</td>
</tr>
<tr>
<td>Injection thickness</td>
<td>entire boundary width</td>
</tr>
<tr>
<td>Surface charge, clay, Su [eq/kg]</td>
<td>0.11$^b$</td>
</tr>
<tr>
<td>Specific surface area, clay $A$, [m$^2$/g]</td>
<td>37</td>
</tr>
<tr>
<td>Mean cation exchange capacity, sand, $CEC^{ex}$ [meq/L]</td>
<td>1.1</td>
</tr>
<tr>
<td>Selectivity coefficients of ion exchange, $logK_{i/Na}$</td>
<td>0.2$^c$</td>
</tr>
</tbody>
</table>

$^a$In Setup A, the inflow boundary was considered along the thickness of the top sandy layer (red line, Fig. 1a).

$^b$In chemical heterogeneity cases, 10% of this value was assumed to be allocated for ion exchange.

$^c$The first and the second values refer to $^{22}$Na$^+$ and Cs$^+$, respectively.

3.3 Simulation scenarios

We performed a series of numerical experiments to analyze the effects of physical, electrostatic and chemical processes, and their associated heterogeneity during multicomponent transport of charged solutes in complex sandy-clayey domains. These simulations are specifically targeted to identify the relevance of the charge induced mechanisms within clay’s nanopore during diffusive/dispersive mass transfer through sandy-clayey interfaces. In all numerical tests we consider a suite of tracer species, containing different charge and diffusion coefficients (Table 3): tritiated water (HTO), $^{22}$Na$^+$, Cs$^+$, and I. These particular species were extensively studied in the investigations of contaminant transport in clay and nuclear waste repositories involving both laboratory and field experiments (e.g., Appelo et al., 2008; 2010; Glaus et al., 2007; 2013; Tachi and Yotsuji, 2014). Such combination of tracer species allows performing a systematic analysis of the impact of charge effects on charge neutral, positively charged, and negatively charged solute species. The numerical
experiments presented in the study can be categorized into two main types depending on the conceptualization of the problem:

(i) *Forward diffusion (FD)*, which refers to the diffusivedispersive mass-transfer of the solute species from the high-permeability sandy matrix to the low-permeability clay inclusions. This problem can be viewed as the long-term loading of contaminants into low-permeability zones during contaminant transport in heterogeneous groundwater flow systems containing sandy-clayey formations. The simulations of this category were performed by continuously injecting the above mentioned tracer species along the entire cross section of the inlet boundary in Setup B and C, and through the thickness of the upper sandy aquifer in Setup A, respectively (red vertical lines, Fig. 1a). As initial condition, the domains were considered to be pristine and none of the solutes were initially present.

(ii) *Back diffusion (BD)*, which focuses on diffusiondispersion dominated mass-transfer of dissolved solutes from the low-permeability clay inclusions to the background sandy matrix. This type of problem is common at contaminated sites where contaminants have been flushed from the permeable matrix but are trapped in low-permeability zones. Such zones act as long-term secondary sources and slowly release the stored contaminants to the more permeable sandy matrix. The back diffusion simulations were performed by considering an initial equilibration of the clay inclusions with the above mentioned tracer species as the model initial condition, and the continuous injection of tracer-free solution at the inlet boundaries (Fig. 1a).

In both cases the tracer-free solution is assumed to have a simple composition with only NaCl as dissolved solutes. The schematics of the boundary and initial conditions of these two types of simulations are provided in Fig. S1 (Supplementary Material), whereas Table 3 reports the
composition of the initial and boundary solutions in different simulations along with the self-diffusion coefficients of the tracer species.

Table 3: Compositions of inflow and initial solutions in the simulations.

<table>
<thead>
<tr>
<th>Species</th>
<th>Forward diffusion (FD)</th>
<th>Back diffusion (BD)</th>
<th>Self-diffusion coefficient, $D_{aq,i}$ (m$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Inflow (M)</td>
<td>Initial (M)*</td>
<td>Inflow (M)</td>
</tr>
<tr>
<td>pH</td>
<td>7</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>HTO</td>
<td>$10^{-3}$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$^{22}\text{Na}^+$</td>
<td>$10^{-3}$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Cs$^+$</td>
<td>$10^{-3}$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>I$^-$</td>
<td>$10^{-3}$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>0</td>
<td>$10^{-3}$</td>
<td>$10^{-3}$</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>0</td>
<td>$10^{-3}$</td>
<td>$10^{-3}$</td>
</tr>
</tbody>
</table>

*Composition of the entire domain and only clay inclusions for forward and back diffusion, respectively
#from Cussler (2009)

For each of these problem categories, we consider three different modeling scenarios specifically focusing on the different combinations of spatially variable physical, electrostatic, and chemical properties in the individual simulation domains. These scenarios involved sequential levels of complexity in terms of incorporating different mechanisms, and can be divided as:

1. **Physical heterogeneity** ($P$) scenario considers only the spatially variable distribution of physical properties such as hydraulic conductivity ($K$), flow velocity ($v$) and dispersion coefficients ($D_L$ and $D_T$) but ignores the electrostatic mechanisms, originated by the charge of ionic species and/or clay surface, and chemical reactions. This scenario can be considered representative of conventional high-resolution solute transport simulations, and is modeled with a single-continuum and a Fickian formulation considering the compound-specific local diffusion/dispersion terms.

2. **Physical and electrostatic heterogeneity** ($P/E$) scenario, where we consider heterogeneous distribution of both the physical and electrostatic properties (Fig. 2a-c, Table 4). In addition to the physical transport processes with inhomogeneous velocity field, these simulations explicitly take into account the diffuse layer mechanisms within clay inclusions as well as ion-ion...
electrostatic interactions, and are performed with the multi-continua and Nernst-Planck based formulation.

3. **Physical, electrostatic and chemical heterogeneity (P/E/C)** scenario is basically an extension of the previous case (P/E), and includes also the heterogeneity associated with chemical reactions in addition to solute transport and charge-driven diffuse layer and electrostatic processes. Specifically, we focus on ion exchange reactions and consider a heterogeneous field of the cation exchange sites (CEC\textsuperscript{Ex}) generated by utilizing a negative correlation with the hydraulic conductivity values (Fig. 2d-f, Table 4). The particular ion exchange reactions that are considered in these simulations can be written as:

\[
\begin{align*}
^{22}\text{Na}^+ + \text{NaX} &\rightarrow ^{22}\text{NaX} + \text{Na}^+ \\
\text{Cs}^+ + \text{NaX} &\rightarrow \text{CsX} + \text{Na}^+
\end{align*}
\]  

The last two scenarios (P/E, P/E/C) represent a novel reactive transport description that is possible with the multi-continua based simulator, MMIT-Clay, whereas the first scenario (P) represents classic high-resolution solute transport simulations in heterogeneous fields. Table 4 lists a complete set of the numerical experiments performed in Setup A, B, and C, and all these simulations were run for a period of 10 years. A unique scenario ID is reported in Table 4 for each simulation and is consistently used throughout the paper.

Table 4. Description of all the simulation scenarios in different heterogeneous domains.

<table>
<thead>
<tr>
<th>#</th>
<th>Problem type</th>
<th>Setup</th>
<th>Scenario ID</th>
<th>Heterogeneous distribution of properties</th>
<th>Model formulation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Physical</td>
<td>Electrostatic</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td>FD-A-P</td>
<td>√</td>
<td></td>
<td>Single</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>A</td>
<td>FD-A-P/E</td>
<td>√</td>
<td>Multi</td>
</tr>
<tr>
<td>3</td>
<td>Forward diffusion</td>
<td>FD-A-P/E/C</td>
<td>√</td>
<td>√</td>
<td>Multi</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>FD-B-P</td>
<td>√</td>
<td></td>
<td>Single</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>B</td>
<td>FD-B-P/E</td>
<td>√</td>
<td>Multi</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>FD-B-P/E/C</td>
<td>√</td>
<td>√</td>
<td>Multi</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>C</td>
<td>FD-C-P</td>
<td></td>
<td>Single</td>
</tr>
</tbody>
</table>
4. RESULTS AND DISCUSSION

For each individual heterogeneous domain, we performed three distinct types of simulations incorporating different combinations of the heterogeneous distributions of physical, electrostatic and chemical properties. The results obtained from these numerical simulations are interpreted in this section from the perspective of mass-exchange between the low- and high-permeability zones, contaminant storage within (and release from) the low-permeability clay inclusions. In the following, we present the main results illuminating the mechanisms controlling transport of the different species, whereas additional results for each individual simulation scenarios are reported in the Supplementary Material.

4.1 Transport in a mildly heterogeneous sandy domain with an underlying clay layer (Setup A)

In this setup described in Fig. 1a and Table 1, the mildly heterogeneous upper aquifer is composed by permeable sandy material, whereas the underlying clay aquitard is negatively charged. Due to the low hydraulic conductivity the flow velocity is negligible in the bottom clay layer, hence this layer is bypassed by most groundwater flow as illustrated in Fig. 1a,d. Therefore, the mass transport
between the sandy aquifer and the clay layers is mainly dominated by the diffusive/dispersive mechanisms.

As outlined in Section 3.3, we consider six individual simulation scenarios in Setup A, divided into the two different problem types of forward and back diffusion. Fig. 3 illustrates the flux-averaged breakthrough curves of the different tracers at the right boundary of the domain (upper row panels), and the spatial profiles of the total concentration in both subcontinua ($FW$ and $DL$) within the clay inclusion along the longitudinal direction (lower row panels) for all the scenarios focusing on the forward diffusion problem ($FD$) in Setup A (i.e., $FD$-$A$-$P$, $FD$-$A$-$P/E$ and $FD$-$A$-$P/E/C$). The total concentration ($c^{All}$) for a species is defined as:

$$c^{All}_i = c^{FW}_i + c^{DL}_i.$$  \hfill (16)

The breakthrough curves of the uncharged species (HTO) are almost identical in all scenarios despite the different physical, chemical and electrostatic properties in the individual cases (Fig. 3a). A very similar behavior is also observed for the anionic tracer ($I^-$), as shown in Fig. 3b. Such outcomes can be explained by the fact that the charge-neutral species is not affected by the electrostatic mechanisms at the clay’s surface or by the ion exchange reactions in the entire domain. In addition, the anions are largely excluded from the diffuse layer due to electrostatic repulsion and are also inert with respect to the cation exchange reactions described in Section 3.3. Therefore, the breakthrough curves of these two species do not show much variation in the different scenarios. In contrast, the cationic species ($^{22}$Na$^+$ and Cs$^+$) exhibit distinct patterns in their breakthrough curves with differences both in the arrival times and tailings’ concentrations (Fig. 3c-d). In comparison with the only physical heterogeneity case (solid blue lines, $FD$-$A$-$P$), slightly smaller tailings’ concentrations are observed in the breakthrough curves of both cations in the electrostatic (dashed-dotted lines, $FD$-$A$-$P/E$) and chemical (dashed lines, $FD$-$A$-$P/E/C$) heterogeneity cases (Fig. 3c-d).
Interestingly, Cs\(^+\) breakthrough is considerably retarded (by more than a year) in the chemical heterogeneity case (FD-A-P/E/C) due to the ion exchange reactions (Fig. 3d), and this retardation front causes the intermediate peak in the \(^{22}\text{Na}^+\) breakthrough (Fig. 3c) due to the replacement of \(^{22}\text{Na}^+\) by Cs\(^+\) on the exchanger.

![Diagram](image)

**Fig. 3.** Flux-averaged breakthrough curves at the outlet (a-d) and spatial profiles of the total concentrations taken at \(t = 10\) years within the clay layer (e-h) for HTO (a, e), \(\Gamma\) (b, f), \(^{22}\text{Na}^+\) (c, g), and Cs\(^+\) (d, h) during the forward diffusion (FD) simulations in Setup A.

The observed behavior in the different species’ breakthroughs is also consistent with the spatial profiles of the total loaded concentrations with an identical profile for the uncharged species in all the scenarios (Fig. 3e). Although the breakthrough curves of \(\Gamma\) are very similar in the different scenarios, the spatial concentrations within clay show a significant variation with approximately five times higher concentrations in the Fickian based physical heterogeneity case (FD-A-P) compared to the other two scenarios (Fig. 3f). This occurs because \(\Gamma\) is electrostatically repelled from the diffuse layer water when electrostatic processes are considered. Consequently, this species can occupy only the free water portion \((f^\text{FW} = 20\%)\) of the clay’s pore water leading to a relatively smaller smaller capacity compared to the other tracers. The uniform concentration profiles in FD-A-P/E and
FD-A-P/E/C are attributed to the fact that the anionic species can quickly reach its maximum capacity (which is 20% of the total porosity) in the clay layer (Fig. 3f). The situation is opposite for the cations because the electrostatic and chemical processes lead to much higher enrichment of these species in the clay inclusion during the transport in FD-A-P/E and FD-A-P/E/C scenarios compared to the physical heterogeneity case (Fig. 3g-h). In the former cases, it is interesting to notice that Cs$^+$ shows higher concentration (Fig. 3h) compared to $^{22}$Na$^+$ (Fig. 3g), which is indeed the result of the relatively higher diffusivity of Cs$^+$ leading to a more enhanced mass-transfer through the sandy-clayey interface (Table 3). Such behavior is remarkable because the effects of molecular diffusion is also dominant in these complex heterogeneous domains. At the end of the simulations ($t = 10$ years), the maximum loaded concentrations in the clay layer were: $9.92 \times 10^{-4}$ mol HTO/L, $9.83 \times 10^{-4}$ mol I$^-$/L, $9.28 \times 10^{-4}$ mol $^{22}$Na$^+$/L and $9.86 \times 10^{-4}$ mol Cs$^+$/L for the physical heterogeneity case; $9.92 \times 10^{-4}$ mol HTO/L, $2.15 \times 10^{-4}$ mol I$^-$/L, $2.27 \times 10^{-2}$ mol $^{22}$Na$^+$/L and $2.87 \times 10^{-2}$ mol Cs$^+$/L for the FD-A-P/E case; and $9.92 \times 10^{-4}$ mol HTO/L, $2.16 \times 10^{-4}$ mol I$^-$/L, $2.27 \times 10^{-2}$ mol $^{22}$Na$^+$/L and $2.92 \times 10^{-2}$ mol Cs$^+$/L for the FD-A-P/E/C case. This implies that the positively charged contaminants are more effectively loaded in the low-permeability inclusions during a forward diffusion within a sandy-clayey system.

Fig. 4 shows the simulation outcomes for the same domain (Setup A) but for the back diffusion problem (BD), which considers that the bottom clay layer is initially loaded with the tracer species and a tracer-free solution is continuously injected at the inflow boundary (Figs. 1 and S1). The breakthrough curves in these back diffusion simulations have generally different trends, compared to the forward diffusion cases, characterized by a fast increase in the outlet concentrations until reaching a peak followed by a gradual decrease involving a long tailing. Such profiles are typical of back diffusion and represent slow release of solute masses from the low-permeability zones to the
more permeable groundwater flow regions (e.g., Parker et al., 2008; Chapman et al., 2012; Rezaei et al., 2013; Yang et al., 2016). While the uncharged species show very similar breakthrough curves in the different scenarios also for these simulations (Fig. 4a), the anionic species shows distinct patterns with a relatively higher peak concentration and less tailing when electrostatic and chemical processes are considered (dashed line for BD-A-P/E and dashed-dotted line for BD-A-P/E/C, Fig. 4b). The cationic breakthrough curves show remarkable differences among the different scenarios, where outlet concentrations are orders of magnitude higher in the simulation considering only physical heterogeneity but ignoring the electrostatic and chemical processes (solid lines, BD-A-P, left axes) compared to the other two cases incorporating the charge and/or reaction mechanisms (dashed-dotted and dashed lines, right axes, Fig. 4c-d).

Fig. 4. Flux-averaged breakthrough curves of HTO (a), I⁻ (b), ^{22}Na⁺ (c, left axis for P, right axes for P/E and P/E/C), and Cs⁺ (d, left axis for P, right axes for P/E and P/) at the outlet of the domain during the back diffusion (BD) simulations in Setup A.

Fig. 5 shows the 2-D concentration distributions (a-l) and the total flux maps (m-t) for BD-A-P (first and fourth row panels) and BD-A-P/E (second, third and fifth row panels) scenarios. The plumes of the different tracer species confirm that solute masses are released from the clay layer mainly by diffusive/dispersive mass-transfer at the interface with the sandy aquifer. The flux maps are particularly helpful for understanding the breakthrough behavior of the different solutes. In Fig. 5 we consider the transverse component of the overall diffusive/dispersive fluxes in all the porosity domains:
\[ \boldsymbol{J}^{\text{All}}_{TJ} = f^{\text{FW}} \boldsymbol{J}^{\text{FW}}_{TJ} + f^{\text{DL}} \boldsymbol{J}^{\text{DL}}_{TJ}. \] (17)

Fig. 5. 2-D plumes of different solutes (a-l), and maps of the transverse component of the total fluxes for different species (m-t) in all subcontinua during the transport incorporating back diffusion (BD) of tracer species in the heterogeneous Setup A \((t = 200 \text{ days})\). Flow direction is from left to right.

The fourth row panels represent the transverse flux maps for the physical heterogeneity case (BD-A-P), whereas the bottom row panels show the fluxes of different species in the physical and electrostatic heterogeneity scenario (BD-A-P/E). It is evident that HTO shows an identical distribution of the flux components in both scenarios with an average value of \(1.42 \times 10^{-13} \text{ mol/m}^2\text{/s}\) (Fig. 5m,q). However, the anion (I) flux increases by approximately 112\% (with average fluxes being \(2.53 \times 10^{-14}\) and \(5.37 \times 10^{-14}\) mol/m\(^2\)/s in BD-A-P and BD-A-P/E scenarios, respectively) when the diffuse layer processes are considered (i.e., in BD-A-P/E, Fig. 5r). This is due to the negatively charged surface of clay, which electrostatically repels the anions leading to a comparatively faster release of I from the clay inclusion in this scenario (Fig. 5b,f) as also reflected in the breakthrough curves in Fig. 4b. In contrast, the cation fluxes decrease by three orders of magnitude (i.e., 1480-
fold for $^{22}\text{Na}^+$, and 1567-fold for Cs$^+$) in BD-A-P/E, where the electrostatic mechanisms are considered (Fig. 5o-p,s-t). This is indeed indicative of the extremely enhanced retention of these species compared to the only physical heterogeneity scenario (BD-A-P). Such behavior is caused by the screening of the positively charged species in the diffuse layer to counter balance the surface charge in BD-A-P/E, and this ultimately inhibits the release of $^{22}\text{Na}^+$ and Cs$^+$ from the clay layer by diffusive/dispersive mass-transfer as observed in the case of BD-A-P. It is also interesting to note that among the cations, Cs$^+$ shows comparatively higher flux magnitudes in both scenarios (i.e., average fluxes of $5.92\times10^{-11}$ and $3.99\times10^{-14}$ mol/m$^2$/s for $^{22}\text{Na}^+$ and $1.02\times10^{-10}$ and $6.51\times10^{-14}$ mol/m$^2$/s for Cs$^+$ in BD-A-P and BD-A-P/E, respectively; Fig. 5o-p,s-t) because of a higher diffusion coefficient (Table 3), and this effect is also reflected in the breakthrough curves with Cs$^+$ having a relatively higher peak concentration (solid and dashed-dotted lines, Fig. 4c-d). However, in the chemical heterogeneity case (BD-A-P/E/C) such effect is not observed in the breakthroughs because the transport is more dominated by the ion exchange reactions, which consider a hundred-fold higher affinity of Cs$^+$ (Table 2) towards the solid phase compared to $^{22}\text{Na}^+$ (dashed lines, Fig. 4c-d). These results have important implications in contaminant back diffusion and remediation since the electrostatic interactions strongly impact the mass release and the persistence of the plumes.

4.2 Transport in a heterogeneous binary field with multiple clay inclusions (Setup B)

This setup involves a 20 m × 2 m (L×W) binary sandy-clayey domain with multiple random low-K inclusions embedded within a sandy matrix (Fig. 1b,e). The same set of simulations focusing on the forward and back diffusion problems and by considering different levels of heterogeneity were also performed in this domain (Table 4, Fig. 2b,e). The boundary and initial conditions as well as the transported species in the corresponding simulations in this setup were similar to the ones of Setup
A as presented in the previous section (Section 3.3, Fig. S1, Supplementary Material). Fig. 6 shows the multicomponent ionic transport simulation results for the forward diffusion problem in the physically, electrostatically and chemically heterogeneous scenario (FD-B-P/E/C), whereas the results of the other two simulation scenarios (i.e., FD-B-P, FD-B-P/E) are reported in the Supplementary Material (Fig. S6). Due to the complex pattern of the streamlines (Fig. 1b) and the spatially variable distribution of the seepage velocities (Fig. 1e), the plumes of the different species in the free porosity take irregular shapes characterized by a diverging trend around the clay inclusions (first column panels, Fig. 6).

Fig. 6. 2-D concentration maps of HTO (a-c), \( I^- \) (d-f), \( ^{22} \text{Na}^+ \) (g-i), and Cs\(^+\) (j-l) in free water (a, d, g, and j), diffuse layer (b, e, h, and k), and exchanger (c, f, i, and l) after 200 days during the forward diffusion (FD) simulation incorporating physical, electrostatic, and chemical mechanisms in Setup B (FD-B-P/E/C). Flow direction is from left to right.

The effects of the electrostatic heterogeneity, involving negative surface charge at the clay inclusions and zero charge in the surrounding sandy matrix (Fig. 2b), are also clearly evident in the distinct plume shapes for the uncharged and charged species in free water (first column panels, Fig.
6) and diffuse layer (second column panels, Fig. 6) porosities. As the uncharged species is not influenced by the electrostatic properties, HTO travels similarly both in the free water and diffuse layer, and this leads to the same concentration in both subcontinua at the inclusions (Fig. 6a,b). In contrast, the anion is clearly depleted and the cations are enriched in the diffuse layer as reflected in their orders of magnitude lower (Fig. 6e) and higher (Fig. 6h,k) concentrations in this charged subcontinuum, respectively, compared to the corresponding free water concentrations at the clay inclusions (e.g., Fig. 6d,g,j). Such diffuse layer composition is illustrative of a charged solution, which is also demonstrated in the charge balance maps in Supplementary Material (Fig. S13).

Interestingly, the anionic plume propagates faster through the domain compared to the uncharged species because of the electrostatic repulsion from the charged surfaces (Fig. 6a,d), and this kind of behavior was also observed in a previous field study (Gvirtzman and Gorelick, 1991). The cationic plume shows the opposite trend, with retarding fronts, compared to the HTO plume due to the electrostatic attraction towards the clay's diffuse layer (Fig. 6a,g,j). The impact of the chemical heterogeneity (Fig. 2e) also shows a similar pattern, as observed in the diffuse layer, involving no effects for HTO and I but enrichment of the cationic concentrations in the exchanger phase due to ion exchange reactions (third column panels, Fig. 6). Among the cations, a chromatographic separation of the solute plumes is clearly visible as Cs$^+$ replaces $^{22}$Na$^+$ on the solid phase along the flow distance (Fig. 6i,l).

Fig. 7 illustrates the flux-averaged breakthrough curves obtained from both the forward (top row panels) and back (bottom row panels) diffusion simulations under different heterogeneous conditions. Although the 2-D concentration maps during transport in both the forward (Fig. 6) and the back diffusion (Fig. S6, Supplementary Material) problems show highly irregular shapes, the breakthrough curves have somewhat regular shapes for the different solute species (Fig. 7). In the
forward diffusion simulations, solute breakthroughs show a trend with long term tailing, which is indicative of mass-exchange limitations between mobile and (partially) immobile zones (Fig. 7a-d). HTO and I\(_-\) show a similar pattern in the breakthrough curves compared to the ones observed in the previous domain (Setup A): i.e., no influence on the uncharged tracer in all scenarios, sharper concentration profiles and higher release of the anion in the forward and back diffusion simulations, respectively, when electrostatic and/or chemical heterogeneity are included (Fig. 7a-b,e-f). In contrast, the cationic species appear to retain more in the diffuse layer during the forward diffusion simulations in this particular domain as reflected in the higher differences in the breakthrough tailings’ concentrations between the different scenarios (i.e., FD-B-P and FD-B-P/E, FD-B-P/E/C) in Fig. 7c-d compared to the ones observed in Fig. 3c-d. The retardation of Cs\(^+\) concentration front is visible in both scenarios, with a relatively slower front (retarded by almost three years) in this domain compared to Setup A, where chemical heterogeneity was included (Fig. 7d,h). These effects are also consistent with the 2-D concentration maps as observed in Fig. 6 (third column panels).

Fig. 7. Flux-averaged breakthrough curves obtained from the forward (FD, a-d) and back diffusion (BD, e-h) simulations for HTO (a,e), I\(_-\) (b,f), \(^{22}\)Na\(^+\) (c, g – left axis: P, right axes: P/E and P/E/C), and Cs\(^+\) (d, h – left axis: P, right axes: P/E and P/E/C) in Setup B. The results are shown for a simulation time of 5 years.
These observed phenomena have implications for contaminant transport and remediation in sandy-clayey domains, and indicate that a particular contaminant is clearly more persistent in such settings when it is positively charged. The observations in Fig. 6 and 7 can be further analyzed by visualizing the different components of the Nernst-Planck fluxes of Eqs. (3) and (4) for different species. Such flux maps allow a closer inspection of the electrostatic effects triggered by the surface charge and the species-species interactions due to their charge. According to Eqs. (3) and (4), the Nernst-Planck flux of a particular ionic species in a subcontinuum entails three different components and can be written as:

\[ J_{i}^{\xi,Tot} = J_{i}^{\xi,Disp} + J_{i}^{\xi,Act} + J_{i}^{\xi,Mig} \tag{18} \]

where \( J_{i}^{\xi,Disp} \), \( J_{i}^{\xi,Act} \) and \( J_{i}^{\xi,Mig} \) [mol/m\(^2\)/s] refer to the purely Fickian diffusive/dispersive flux components, fluxes due to the gradients of activity coefficients, and contribution due to the electrical potential gradients, respectively, and \( J_{i}^{\xi,Tot} \) is the total diffusive/dispersive flux within a subcontinuum \( \xi \). For flow-through simulations, as the ones presented in this section, these flux components have analogous expressions as in Eqs. (3) and (4) but are expressed in terms of hydrodynamic self-diffusion/dispersion coefficients instead of the aqueous diffusion coefficients as explained in Section 2.2. As an example, in Fig. 8 we plot the maps of the transverse component of these different flux contributions in both the free water and diffuse layer porosities for the back diffusion problem involving spatially variable distribution of physical and electrostatic properties (Scenario BD-B-P/E). The panels in the upper four rows represent the flux components in the free water porosity, whereas the panels in the remaining rows show the fluxes within the diffuse layer water. In both subdomains, higher magnitudes of the total fluxes (\( J_{i}^{FW,Tot} \) and \( J_{i}^{DL,Tot} \)) are generally localized directly in the clay inclusions and within their surroundings (panels in the first and fifth row, Fig. 8). Such behavior is expected for the back diffusion problems because the clay inclusions
indeed act as a source for the considered tracer species, and gradually release the solute masses to the surrounding sandy matrix of the domain via diffusive/dispersive mass-transfer. The electromigration fluxes in the free water \( \left( J_{FW,Mig}^{i} \right) \) show a complex pattern containing both positive (red portions) and negative (blue portions) components in the different portions of the solute plumes (third row panels, Fig. 8). Directly at the clay inclusions, the electrical potential induced by the variation in the mobility of different species leads to a deceleration for \( \Gamma \) (negative \( J_{FW,Mig}^{i} \)) and an acceleration for \( ^{22}\text{Na}^{+} \) and \( \text{Cs}^{+} \) (positive \( J_{FW,Mig}^{i} \)) compared to their self-diffusivity (shown in Fig. S14, Supplementary Material). An opposite trend is observed in the direct proximity of these inclusions as well as in their upstream locations, where solute plumes originating from each inclusions are rather unaffected by the processes occurring within the clay (third row panels, Fig. 8).

Fig. 8. Maps of the total fluxes (first and fifth row panels), diffusive/dispersive fluxes (second and sixth row panels), electromigration fluxes (third and seventh row panels), and activity gradient fluxes (fourth and eighth row panels) for HTO (first column panels), \( \Gamma \) (second column panels), \( ^{22}\text{Na}^{+} \) (third column panels), and \( \text{Cs}^{+} \) (fourth column panels) after 200 days for the back diffusion
simulation considering physical and electrostatic processes (BD-B-P/E) in the binary heterogeneous setup (Setup B). The panels in the first to fourth rows represent fluxes in the free water porosity, whereas the panels in the fifth to eight rows represent the fluxes in the diffuse layer porosity.

This behavior was also observed in previous experimental investigations focusing on pH fronts propagation and multicomponent ionic dispersion (e.g., Rolle et al., 2013; Muniruzzaman and Rolle, 2015; 2017). It highlights the importance of Nernst-Planck description of charged species’ transport, which cannot be adequately described with a simple Fickian-based formulation. In the diffuse layer water, the situation is opposite with the positive (red) and negative (blue) $J_i^{DL,Mig}$ contributions for the anions and cations, respectively (seventh row, Fig. 8). The magnitudes of the cationic electromigration fluxes in this subcontinuum are several orders of magnitude higher (average fluxes of $2.14\times10^{-10}$ and $3.33\times10^{-10}$ mol/m$^2$/s for $^{22}\text{Na}^+$ and Cs$^+$) compared to the one of the anion ($5.26\times10^{18}$ mol/m$^2$/s; seventh row) as well as to the total flux components (with average fluxes values of $9.83\times10^{-14}$, $1.05\times10^{-17}$, $8.86\times10^{-18}$ and $1.38\times10^{-17}$ mol/m$^2$/s for HTO, I$^-$, $^{22}\text{Na}^+$ and Cs$^+$, respectively; fifth row) of all the species (Fig. 8). Such outcome is remarkable and implies that the electrostatic interactions with the clay’s charged surface can evidently accelerate or retard the release or loading rates (up to seven orders of magnitude in the investigated cases) of a certain contaminant in charged low-permeability media depending on the contaminant charge. This analysis of the computed exchange fluxes also explains the observed differences in the cationic breakthrough curves (as shown in Figs. 4, 7) obtained from the simulations considering different combinations of physical, electrostatic and/or chemical processes. The activity gradient fluxes are negligible in both subcontinua because none of the simulation scenarios considered in this study involved strong ionic strength gradients (fourth and eighth row, Fig. 8).

4.3 Transport in a heterogeneous domain with multiple clay inclusions (Setup C)
The same set of reactive transport simulations were also performed in Setup C, which is characterized by the same dimensions (20 m × 2 m) and clay inclusions as in Setup B (Fig. 1b-c). The main distinctive feature of this particular domain compared to Setup B is associated to the distribution of physical and chemical properties in the background sandy matrix: i.e., spatially distributed hydraulic conductivities and ion exchange reaction sites in this setup, whereas these properties had a uniform value in the binary domain of Setup B (Fig. 2). Fig. 9 illustrates a comparison between the spatial concentration distribution of the different tracer species obtained from the two back diffusion simulations indicated as BD-C-P (top row panels, considering only physical heterogeneity) and BD-C-P/E (middle and bottom rows panels, considering both the physical and electrostatic heterogeneity) in Table 4. For the case BD-C-P (top row panels), the concentrations of all species show a similar distribution, however, the concentrations of the cations are considerably higher in the low-permeability inclusions.

![Fig. 9. 2-D concentration maps for the physically (BD-C-P, a-d), and physically and electrostatically (BD-C-P/E, e-l): free water concentrations, e-h; diffuse layer concentrations, i-l) heterogeneous back diffusion scenarios in Setup C: HTO (a, e, i), I\(^-\) (b, f, j), \(^{22}\text{Na}^+\) (c, g, k), and Cs\(^+\) (d, h, l). Flow direction is from left to right.](image-url)
In both scenarios, the overall concentration maps appear to be composed of several individual plumes originating from each of the inclusions. It is apparent that HTO shows the same extent of the release of solute mass from the low-\(K\) inclusions in both scenarios, and it also has the same concentration within the different subcontinua in BD-C-P/E (Fig. 9a,e,i). However, the effects of the electrostatic attraction and repulsion within the clay’s diffuse layer are clearly evident for the charged species because the anionic tracer (\(\Gamma\)) shows a relatively faster depletion of iodide concentration and exclusion in the charged porosity within the inclusions in the second scenario (BD-C-P/E) (Fig. 9b,f,j). In the same scenario considering charge effects (BD-C-P/E), the cations are electrostastically pulled by the higher magnitude of the electromigration fluxes in the diffuse layer (as also shown in the seventh row of Fig. 8), and this leads to a considerable inhibition of their displacement through the sandy-clayey interface (Fig. 9g,h,k,l). However, in Scenario BD-C-P such charge driven electrostatic mechanisms are ignored and this allows the positively charged species to be released from the inclusions only by the physical advective-dispersive transport mechanisms (Fig. 9c-d). Such outcome is, in fact, quite significant because upon ignoring these electrostatic mechanisms, which is still a common practice in subsurface simulations, one might extremely under- or overestimate the contaminant storage to (or release from) low-permeability zones during subsurface contaminant transport depending on the charge of the contaminant.

Fig. 10 presents the solute masses within the clay inclusions that are stored and released in the forward (a-d) and back (e-h) diffusion simulations, respectively, at the end of the simulations (10 years). These solute masses \(m_i\) at a particular time are calculated by integrating the concentrations in different subcontinua over the total volume of the low-permeability clay inclusions \(V_{clay}\):

\[
m_i(t) = \int_{V_{clay}} \left[ \theta \left( f^{FW} c_i^{FW}(x,t) + f^{DL} c_i^{DL}(x,t) \right) + (1-\theta) s_i(x,t) \right] dx
\]  \hspace{1cm} (19)
where $s_i^{Ex}$ [mol/L] represents the concentrations in the exchanger phase. Fig. 10 shows the difference between the total masses calculated at the initial and final simulation times (i.e., $\Delta m_i = |m_i(t_{end}) - m_i(0)|$). For the back diffusion problem we normalized the released tracers’ mass from the clay lenses by their initially available mass in these inclusions ($m_i(0)$), whereas in the forward diffusion simulations the loaded/stored mass is normalized by the total capacity of the clay inclusions with respect to the inflow concentrations:

$$m_{capacity} = \int_{V_{Clay}} \left[ \theta \left( f^{FW}_{C,i,in} (x) + f^{DL}_{C,i,in} (x) \exp \left( \frac{z_i F \phi^{DL}}{RT} \right) \right) - (1 - \theta) s_i^{Ex} (x) \right] dx$$

(20)

Clearly, HTO occupies 100% of the total capacity of clay’s pore space after 10 years in all the scenarios considering the forward diffusion problem (Fig. 10a). I shows a similar outcome in the simulation considering only the physical processes (FD-C-P) but only ~20% of the total capacity is filled in the other two scenarios (FD-C-P/E and FD-C-P/E/C) because the anion is excluded from the diffuse layer, which constitutes about 80% of the total pore space of the clay material (Table 2, Fig. 10b). In contrast, the loaded mass for the cations during forward diffusion are significantly smaller (<2% of the total capacity of clay) compared to the anion and charge-neutral species because the absolute capacity of the cations are indeed dependent on the Boltzmann factor ($\exp(-z_i F \phi^{DL}/RT)$) leading to orders of magnitude higher values compared to the other two species (Fig. 10c-d). Interestingly, the stored cationic masses are more than an order of magnitude smaller (i.e., ~0.06% of the total capacity) in the physical heterogeneity case (FD-C-P) than that of other two scenarios (~2% of the total capacity). This implies that the low-permeability inclusions can trap significantly higher contaminant masses under the influence of electrostatic and chemical mechanisms. In the back diffusion simulations, the situation is also similar for HTO: i.e., almost the entire initial mass is released from the clay inclusions by the end of the simulation (Fig. 10e).
Unlike the forward diffusion simulations, ~100% of the initial I mass is released from the inclusions in all the scenarios (Fig. 10f). This is caused by the electrostatic repulsion of this anionic species from the charged pore water of clay. The cations show a similar behavior (i.e., ~100% release of solute mass) in BD-C-P compared to the anionic and uncharged tracers because the mass-exchange takes place only via diffusive/dispersive fluxes in this scenario. However, their release can be electrostatically inhibited (up to 99% for the duration considered here) in the other two cases (i.e., BD-C-P/E and BD-C-P/E/C) in comparison with the physical heterogeneity case (Fig. 10g-h). This suggests that depending on the magnitude of the prevailing electrostatic effects and the charge of a particular species, the total release of contaminant mass from clay inclusions can vary within several orders of magnitudes among different contaminant species leading to remarkably different persistence of contaminant plumes.

![Graphs showing mass release](image)

Fig. 10. Stored solute masses in the low-permeability inclusions during forward diffusion simulations (a-d), and released solute masses from the low-permeability clay inclusions in the back diffusion simulations (e-h) in Setup C.

5. CONCLUSIONS
The presence of low-permeability zones in subsurface systems strongly impacts fluid flow and solute transport processes as they usually lead to high contrasts in various physicochemical properties. In low-permeability media containing micro- to nanopores, in addition to the classic physical mechanisms (e.g., advection, diffusion/dispersion), electrostatic and chemical processes may emerge as the dominant processes controlling the distribution, transport, persistence and remediation of groundwater contaminants. In this study, we presented a detailed investigation to systematically explore the effects of the different level of coupling between these physical, electrostatic, and chemical mechanisms on reactive contaminant transport in two-dimensional, field-scale, heterogeneous sandy-clayey formations. We performed an extensive set of numerical experiments in three distinct heterogeneous domains, and we focused on the storage and release of different charged species in the low-permeability clay inclusions. These experiments involved a sequential level of complexity with different combinations of the heterogeneous distribution of physical, electrostatic, and chemical properties. The simulation results revealed that the charge-induced processes that mainly occur at micro- to nano-scales within the porous media can clearly have outsized impact on field-scale subsurface solute transport. In fact, depending on the species’ charge a particular contaminant can be considerably retarded or accelerated in the low-\(K\) media. In the investigated cases, considerable differences have been observed between the different heterogeneous scenarios, both in terms of diffusive/dispersive fluxes (more than three orders of magnitude faster/slower exchange rates when also electrostatic and chemical heterogeneity are taken into account), as well as mass storage and release within the clay inclusions (relative difference up to 99\% compared to the only physical heterogeneity case). Furthermore, differences were also significant among the different solute species, within a given heterogeneous domain, with relative differences up to 70\% and 80\% for the anionic flux and mass storage, and up to 62\% and 99\% for the cationic flux and mass storage/release, respectively, in comparison with the uncharged
tracer. Therefore, ignoring these electrostatic processes can lead to extreme over- or underestimation of the release and loading of charged contaminants in low-permeability media. In addition, the chemical heterogeneity may also considerably affect subsurface contaminant transport and engineered remediation. The numerical experiments also suggest that such tightly coupled physical, chemical and electrostatic mechanisms and the effects of their spatial distribution cannot be accurately resolved by the classic single porosity subsurface solute transport models but require a multi-continua based reactive transport formulation as used in this study.

The outcomes of this study provide critical insights in advancing the fundamental understanding of multicomponent reactive transport processes in heterogeneous groundwater systems involving sandy-clayey media. We have confined our investigation to predominantly horizontal groundwater flow, whereas vertical flow components may be prominent in natural systems and can impact the magnitude of mass-exchange fluxes through the sandy-clayey interface. Future studies should also address multicomponent ionic transport in other types of low-permeability media containing different minerals (e.g., McNeece and Hesse, 2017; Stolze et al., 2019) and/or higher heterogeneity (e.g., Zhang et al., 2013; Guo and Brusseau, 2017). We envision future research based on the proposed approach and investigating different reactive systems including charged inorganic and organic contaminants (Fakhreddine et al., 2016; McNeece and Hesse, 2017; Molins et al., 2012; Poonoosamy et al., 2016; Prigiobbe and Bryant, 2014; Battistel et al., 2019; Stolze et al. 2019b), exploring the effects of electrostatic interactions also in permeable natural media with complex mineral assemblages (Stolze et al. 2020), investigating the impact of spatially distributed electrostatic and chemical properties in fully three-dimensional systems where physical anisotropy and flow topology may play a major role (Chiogna et al., 2014 and 2015), and assessing the role of spatially distributed diffuse layer processes in engineered systems such as electrokinetic setups for
in situ leaching and contaminant remediation of low-permeability porous media (e.g., Martens et al., 2018; Sprocati et al., 2020; Alizadeh et al., 2019).

Acknowledgments

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Table 1. Geometry and hydraulic parameters used in the generation of heterogeneous flow fields.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Setup A</th>
<th>Setup B</th>
<th>Setup C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Domain size ($L \times W$) [m]</td>
<td>$20 \times 2.20$</td>
<td>$20 \times 2$</td>
<td>$20 \times 2$</td>
</tr>
<tr>
<td>Discretization, $\Delta x/\Delta z$ [m]</td>
<td>$0.4/0.02$</td>
<td>$0.4/0.02$</td>
<td>$0.4/0.02$</td>
</tr>
<tr>
<td>Mean hydraulic conductivity, sandy matrix [m/s]</td>
<td>$9.75 \times 10^{-3}$</td>
<td>$6.14 \times 10^{-4}^{a}$</td>
<td>$6.14 \times 10^{-4}$</td>
</tr>
<tr>
<td>Hydraulic conductivity, clay lenses [m/s]</td>
<td>$6.14 \times 10^{-9}$</td>
<td>$6.14 \times 10^{-9}$</td>
<td>$6.14 \times 10^{-9}$</td>
</tr>
<tr>
<td>Variance, sandy matrix, $\sigma^2_{lnK}$</td>
<td>0.29</td>
<td>-</td>
<td>1.00$^{b}$</td>
</tr>
<tr>
<td>Length scale parameters, $l_x/l_z$</td>
<td>0.56/0.12</td>
<td>2/0.10</td>
<td>2/0.10</td>
</tr>
<tr>
<td>Hydraulic gradient [-]</td>
<td>$5.40 \times 10^{-3}$</td>
<td>$7.80 \times 10^{-4}$</td>
<td>$7.80 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

$^{a}$This setup refers to a binary field, therefore, a uniform value was allocated throughout the sandy matrix.

$^{b}$This value refers to the variance of the original Gaussian kernel (i.e., before creating the clay lenses).
Table 2. Transport, surface, and ion exchange parameters used in all simulations.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average flow velocity [m/d]</td>
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<tr>
<td>Total porosity, sandy matrix [-]</td>
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<tr>
<td>Total porosity, clay lenses [-]</td>
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<tr>
<td>Fraction of free porosity in clay, ( f^W ) [-]</td>
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</tr>
<tr>
<td>Tortuosity, sandy matrix [-]</td>
<td>2.44</td>
</tr>
<tr>
<td>Tortuosity, clay lenses [-]</td>
<td>6.25</td>
</tr>
<tr>
<td>Injection type</td>
<td>continuous</td>
</tr>
<tr>
<td>Injection thickness</td>
<td>entire boundary width(^a)</td>
</tr>
<tr>
<td>Surface charge, clay, ( S_u ) [eq/kg]</td>
<td>0.11(^b)</td>
</tr>
<tr>
<td>Specific surface area, clay ( A_s ) [m(^2)/g]</td>
<td>37</td>
</tr>
<tr>
<td>Mean cation exchange capacity, sand, ( CEC_{Ex} ) [meq/L]</td>
<td>1.1</td>
</tr>
<tr>
<td>Selectivity coefficients of ion exchange, ( \log K_{i/Na} )</td>
<td>0.2(^c)</td>
</tr>
</tbody>
</table>

\(^a\)In Setup A, the inflow boundary was considered along the thickness of the top sandy layer (red line, Fig. 1a).

\(^b\)In chemical heterogeneity cases, 10% of this value was assumed to be allocated to ion exchange.

\(^c\)The first and the second values refer to \(^{22}\)Na\(^+\) and Cs\(^+\), respectively.
Table 3: Compositions of inflow and initial solutions in the simulations.

<table>
<thead>
<tr>
<th>Species</th>
<th>Forward diffusion (FD)</th>
<th>Back diffusion (BD)</th>
<th>Self-diffusion coefficient, $D_{aq} (m^2/s)^{#}$</th>
</tr>
</thead>
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<tr>
<td></td>
<td>Inflow (M)</td>
<td>Initial (M)*</td>
<td>Inflow (M)</td>
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<tr>
<td>pH</td>
<td>7</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>HTO</td>
<td>10$^{-3}$</td>
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<td>0</td>
</tr>
<tr>
<td>$^{22}$Na$^+$</td>
<td>10$^{-3}$</td>
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<td>0</td>
</tr>
<tr>
<td>Cs$^+$</td>
<td>10$^{-3}$</td>
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<td>0</td>
</tr>
<tr>
<td>I$^-$</td>
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<td>0</td>
</tr>
<tr>
<td>Na$^+$</td>
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<td>10$^{-3}$</td>
<td>10$^{-3}$</td>
</tr>
<tr>
<td>Cl$^-$</td>
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<td>10$^{-3}$</td>
<td>10$^{-3}$</td>
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</tbody>
</table>

*Composition of the entire domain and only clay inclusions for forward and back diffusion, respectively

# from Cussler (2009)
Table 4. Description of all the simulation scenarios in different heterogeneous domains.

<table>
<thead>
<tr>
<th>#</th>
<th>Problem type</th>
<th>Setup</th>
<th>Scenario ID</th>
<th>Heterogeneous distribution of properties</th>
<th>Model formulation</th>
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<td>Physical</td>
<td>Electrostatic</td>
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<td>2</td>
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<td>6</td>
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<td>7</td>
<td></td>
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<tr>
<td>8</td>
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<td>FD-C-P/E</td>
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<td>9</td>
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<td>10</td>
<td>Back diffusion</td>
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</tbody>
</table>
Muhammad Muniruzzaman: Conceptualization; Investigation; Data Curation; Software; Writing – Original Draft; Funding acquisition.

Massimo Rolle: Conceptualization; Investigation; Validation; Writing – Review & Editing; Supervision; Funding acquisition.
Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:
HIGHLIGHTS (3 to 5 points, max 85 characters each)

- Physical, chemical and electrostatic effects on transport in low-permeability media
- Multicontinua-based approach to model charge interactions at clay surfaces
- Numerical tests in heterogeneous sandy-clayey domains with multilevel complexity
- Impact of microscopic diffuse layer mechanisms on macroscopic mass transfer
- Analysis of solute breakthroughs, mass storage/release, and Nernst-Planck fluxes