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HIGHLIGHTS

- Novel multidimensional multicomponent reactive transport approach for EK;
- Validation with analytical, numerical and experimental data;
- Nernst-Planck-Poisson equations to account for charge interactions and electroneutrality;
- Simple analytical function proposed to estimate limitation in amendment delivery;

**Modeling electrokinetic transport and biogeochemical reactions in porous media:
a multidimensional Nernst-Planck-Poisson approach with PHREEQC coupling**

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ABSTRACT

Electrokinetic techniques (EK) have been proposed and applied in different fields of science and engineering to enhance solute transport and species mobility in subsurface porous media. Modeling of EK requires a comprehensive approach allowing the description of the complex interplay between physical, chemical and biogeochemical processes occurring in EK applications. We propose a multidimensional modeling approach that allows the integrated description of fluid flow, solute transport (including electromigration and electroosmosis), Coulombic interactions between transported species, and a wide range of kinetic and equilibrium reactions. The proposed modeling tool, NP-Phreeqc-EK, is a coupling between COMSOL Multiphysics, which is used to solve fluid flow and solute transport in saturated porous media based on a Nernst-Planck-Poisson formulation, and PhreeqcRM, used to solve geochemical reactions. We illustrate the capabilities of NP-Phreeqc-EK with selected benchmarks in domains with different dimensions (1D, 2D and 3D). The results of the model are successfully compared with analytical solutions, numerical simulations with other software, and data from previously published EK-experiments. The outcomes of this study show the flexibility of the approach in simulating electrokinetic reactive transport processes in saturated porous media and highlight the importance of Coulombic interactions in EK applications. Such electrostatic interactions can strongly impact the performance of EK techniques since they affect the displacement velocities of charged species and can limit the maximum concentration of amendments that can be delivered through electromigration.

1. Introduction

Electrokinetic techniques are used in different fields of science and engineering (Lima et al., 2017; Ribeiro et al., 2016). Focusing on environmental subsurface applications, electrokinetic remediation (EKR) is a technology that uses a low-intensity electric field produced by electrodes placed in the ground to mobilize and remove contaminants and/or to enhance the delivery of amendments (Reddy and Cameselle, 2009). In recent years, this technology has received increasing attention due to the ability to remove both organic and inorganic contaminants from low-permeability soils and sediments where other technologies may fail. Strategies for the removal of organic contaminants can involve the delivery of oxidants such as permanganate to promote in situ chemical oxidation (EK-ISCO) (Chowdhury et al., 2017; Reynolds et al., 2008; Roach and Reddy, 2006), as well as the delivery of amendments such as lactate, nitrate and sulfate to favor biodegradation (EK-Bio) (Lee et al., 2007; Lohner et al., 2008; Mao et al., 2012; Wu et al., 2012b). For the removal of heavy metals, common approaches involve the generation of an acid front at the anode to promote desorption of the contaminants from the solid matrix (Masi et al., 2016; Yeung and Gu, 2011b).

The main transport mechanisms induced by the application of an electric field are: (i) electromigration, consisting in the displacement of charged species towards the electrode of opposite charge by electrostatic forces, and (ii) electroosmosis, resulting in a net movement of fluid flow as a consequence of the excess of charge adhered to the mineral surfaces, thus affecting also non-charged species (Acar and Alshawabkeh, 1993). Electrolysis reactions in proximity of the electrodes also play a key role as the generation of an acidic front at the anode and an alkaline front at the cathode can have a strong

impact on the system geochemistry, and can favour or prevent chemical reactions such as mineral precipitation and dissolution.

Numerical models have been recognized as important tools for electrokinetic remediation since they are instrumental for the fundamental understanding of the governing physical and geochemical processes, as well as for the design, optimization and control of EKR systems (Alshawabkeh, 2009; Pham and Sillanpää, 2015; Yeung, 2011a). Different modeling approaches have been proposed to simulate electrokinetic transport at the small scale (Alizadeh and Wang, 2019; Pennathur and Santiago, 2005) and in a number of larger scale applications with different levels of complexity (Alshawabkeh and Acar, 1996; Amrate and Akretche, 2005; Choi and Lui, 1995; Jacobs et al., 1994; López-Vizcaíno et al., 2017; Mascia et al., 2007; Paz-García et al., 2011; Ribeiro et al., 2005; Yu and Neretnieks, 1996). Although the majority of the models have been developed for 1-D geometries to support the interpretation of laboratory experiments, there are also some applications in multiple dimensions (e.g., Rubio-Nieblas et al., 2014; Wu et al. 2012b). The most advanced simulators typically include the coupling of the physical mass transfer processes with geochemical databases to simulate EKR in saturated porous media (e.g., Wu et al., 2012a; Rasouli, 2016; Masi et al., 2017). Despite the increasing importance of numerical simulators for environmental applications of electrokinetic techniques and the recent advances in the development of these tools, a modeling approach capable of coupling the physics of fluid flow and mass transfer processes, with the biogeochemistry of subsurface reactions, and with the electrostatic interactions between charged species in porous media in multiple dimensions is still missing.

In the present study we aim to address this research gap by proposing a multidimensional approach to model multicomponent electrokinetic transport and reactions in saturated porous media. The distinguishing features of the proposed model, NP-Phreeqc-EK, are: (i) the solution of the Nernst-Planck-Poisson equations to accurately describe the Coulombic interactions coupling the displacement of charged species in porous media and to comply with the electroneutrality condition, and (ii) the flexible integration with a geochemical database allowing the simulations of kinetic and equilibrium reactions occurring both in the pore solution and at the solid/liquid interface. The approach is implemented as a coupling between COMSOL Multiphysics[®], used to simulate fluid flow, solute mass transfer and electrostatic processes, and PHREEQC (Parkhurst and Appelo, 2013), used as geochemical engine. Selected electrokinetic transport problems are used as benchmark examples to illustrate the capabilities and to validate the proposed modeling approach. Simulations are carried out for 1-D, 2-D and 3-D domains considering both conservative and reactive scenarios of electrokinetic transport and comparing the outcomes of NP-Phreeqc-EK with analytical, numerical and experimental results. We also illustrate the ability of the proposed approach to predict the coupled transport of charged species with different mobilities and the limiting effects of background solutions and their ionic strength on the delivery of amendments during EKR. Concerning this important limitation, we propose a simple mathematical expression to estimate the maximum concentration of a reactant that is possible to deliver by electromigration in EKR applications in saturated porous media.

2. Modeling approach

2.1 Governing equations

Coulombic interactions affect the displacement of charged species in porous media and need to be considered for a rigorous description of conservative and reactive transport. The mechanisms of Coulombic interactions have been described in detail by several authors in the geochemical literature on multicomponent ionic diffusion (Appelo and Wersin, 2007; Boudreau et al., 2004; Cussler, 2009). Recent experimental investigation has demonstrated the macroscopic impact of such electrostatic interactions also in advection-dominated regimes and introduced the concept of multicomponent ionic dispersion (Muniruzzaman et al., 2014; Muniruzzaman and Rolle, 2015, 2017; Rolle et al., 2013b). It is now possible to describe Coulombic interactions, under natural transport conditions, with several reactive transport simulators (e.g., Meeussen, 2003; Muniruzzaman and Rolle, 2016; Parkhurst and Appelo, 2013; Rasouli et al., 2015; Rolle et al., 2018; Steefel et al., 2014).

The fundamental starting point to describe the transport of charged species is their diffusive displacement that depends on the electrochemical potential μ , which for an ion i reads as:

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

Where μ_i^0 is the electrochemical potential in standard conditions, a_i is the activity of the ion in solution, z_i is its valence, R is the ideal gas constant, T is the temperature, F is the Faraday's constant and Φ is the electrostatic potential. Considering the spatial gradient of the electrochemical potential, the flux of the i -th species J_i in aqueous solution can be described by the Nernst-Planck equation (Appelo and Wersin, 2007; Cussler, 2009):

$$J_i = J_i^{Dif} + J_i^{Act} + J_i^{Mig} = -D_i^{aq} \nabla c_i - D_i^{aq} c_i \nabla \ln(\gamma_i) - D_i^{aq} \frac{z_i F}{RT} c_i \nabla \Phi \quad (2)$$

where J_i^{Dif} is the diffusive flux, D_i^{aq} is the aqueous diffusion coefficient, γ_i is the activity coefficient, J_i^{Act} is the activity flux, $\nabla \Phi$ is the electric potential gradient and J_i^{Mig} is the migration flux.

In porous media the Nernst-Planck equations assume a formulation formally equivalent to Eq. 2 but in which the free aqueous diffusion coefficient is substituted by the pore diffusion coefficient ($D_i = D_i^{aq} \tau$, where τ is the tortuosity) or, under flow-through conditions, by the hydrodynamic dispersion coefficient (Rolle et al., 2018). As shown by recent pore scale and experimental investigations (Rolle et al., 2012, Hochstetler et al. 2013, Ye et al., 2015), the latter is strongly affected by the solute aqueous diffusion also in advection and strongly advection dominated regimes.

In the presence of advective processes in porous media such as groundwater flow or electroosmosis, the Nernst-Planck equation can also be expressed in an extended form (e.g., Rasouli et al., 2015) and the total flux of a charged species can be written as:

$$J_i^{Tot} = \underbrace{-n D_i \nabla c_i}_{J_i^{Dif}} \underbrace{-n D_i c_i \nabla \ln(\gamma_i)}_{J_i^{Act}} \underbrace{-n D_i \frac{z_i F}{RT} c_i \nabla \Phi}_{J_i^{Mig}} \underbrace{+ q^* c_i}_{J_i^{Adv}} \quad (3)$$

in which $q^* c_i$ represents the advective flux of species i and n is the accessible porosity.

In electrokinetic applications, the applied electric field induces the solute mass transfer processes of electromigration and electroosmosis. In Eq. 3 the former is accounted for by the migration flux whereas electroosmosis can be included in the advective flux since the specific water flux q^* can be written as $q^* = q + u_{eo}$ where q is the specific discharge

resulting from piezometric head differences and $\mathbf{u}_{eo}$ is the electroosmotic velocity. In saturated porous media, $\mathbf{q}$ is obtained from the solution of the continuity equation and Darcy's law:

$$\mathbf{q} = \frac{K_h}{\mu} \nabla h \quad (4)$$

where K_h is the hydraulic conductivity, μ is the dynamic viscosity, and ∇h is the piezometric head gradient.

According to the Helmholtz-Smoluchowski theory, the electroosmotic velocity can be described as (Al-Hamdan and Reddy, 2005) $\mathbf{u}_{eo} = -k_{eo} \nabla \Phi$, in which k_{eo} is the electroosmotic permeability, typically in the range of $10^{-8} - 10^{-9} \text{ m}^2/(\text{V}\cdot\text{s})$ for natural soil types at near-neutral pH (Casagrande, 1952).

The governing multicomponent ionic transport equation is given by a material balance:

$$\frac{\partial(nc_i)}{\partial t} + \nabla \cdot \mathbf{J}_i^{Tot} = r_i \quad (5)$$

in which r_i is the reactive source/sink term.

The solution of the governing transport equations based on a Nernst-Planck formulation but neglecting electrostatic interactions between charged species and, thus, their coupled displacement is an approach that has been frequently adopted in electrokinetic applications. This method, defined as the Single Species Model (SSM) by Krabbenhøft and Krabbenhøft (2008), implicitly assumes that the movement of an ion is independent from the other charged species in solution. This approach is simple, and under certain conditions, it could represent a reasonable approximation. However, it does not rigorously consider the charge balance and appears to be in contrast with experimental

observations in which Coulombic interactions occur between ions characterized by different diffusive velocities in order to maintain an overall charge-balanced solution at the Darcy's scale. The electroneutrality condition, commonly expressed as $\sum z_i c_i = 0$, is a macroscopic relation observed in electrolytic solutions that must be also valid locally in every point of the continuum representation of the porous medium. For the purposes of this study, in which the description of electrokinetic processes in porous media is performed with a continuum approach, the continuous validity of the electroneutrality condition ensures that as a result of a charge imbalance of the system caused by an imbalanced source or sink (e.g., due to electrolysis reactions, different displacement velocities of the different ions, or the presence of a charged surface) the other ions in solution are able to migrate to balance the charge and to maintain electroneutrality in every point of the domain. This principle is ensured relating Gauss' law with the definition of electric charge density ($\rho_e = F \sum z_i c_i$), which leads to the Poisson's equation for electrostatics (MacGillivray, 1968; Sastre and Santaballa, 1989):

$$\nabla^2 \Phi = \frac{\rho_e}{\epsilon} \quad (6)$$

where ϵ is the absolute permittivity of the medium.

The system of Eqs. 3, 5, and 6 represents the so-called Nernst-Planck-Poisson equations (NPPE) that describe the coupled displacement of charged species in saturated porous media.

The description of the system also requires considerations about the electric current and the charge balance. Considering that an electric current is defined as the flow of charged

species, it is possible to associate the transport of ions in solution with electrostatic definitions (Pamukcu, 2009). Therefore, as a consequence of the ions' charge, a flux of ions corresponds to an electric current flux $\mathbf{I}$, indicated also as current density:

$$\mathbf{I} = F \sum_{i=1}^N z_i \mathbf{J}_i^{Tot} \quad (7)$$

Note that this equation assumes that the dominant contribution affecting the electric potential distribution is the conductivity of the pore water solution. When also the conductivity of the solids is important, an additional term depending of the apparent electrical conductivity of the soil should be considered (e.g., Jacobs and Probst, 1996; Revil 2017). By expressing the different components of the total flux in the pore water solution, the extended form of Eq. 7 can be written as:

$$\mathbf{I} = -F \sum_{i=1}^N z_i n D_i \nabla c_i - F \sum_{i=1}^N z_i n D_i c_i \nabla \ln(\gamma_i) - \left(F^2 \sum_{i=1}^N z_i^2 \frac{n D_i}{RT} c_i \right) \nabla \Phi + F \mathbf{q}^* \sum_{i=1}^N z_i c_i \quad (8)$$

Following the validity of the charge conservation condition, the continuity condition in terms of charges can be expressed as:

$$F \sum_{i=1}^N z_i \frac{\partial (n c_i)}{\partial t} + \nabla \cdot \left(F \sum_{i=1}^N z_i \mathbf{J}_i^{Tot} \right) = F \sum_{i=1}^N z_i r_i \quad (9)$$

In EK systems the current applied at the electrodes also creates different redox conditions at the electrodes' surfaces. The resulting competitive electrolysis reactions at the electrodes will be influenced by their reduction potentials, in which the reaction with the

highest potential value occurs at the anode and the one with the lowest at the cathode (Paz-García, 2012). Assuming only water reduction at the cathode and oxidation at the anode, the redox equations are respectively:

and:

These reactions are generally modeled as fluxes $J_{H^+}^{el}$ at the electrodes according to Faraday's law (Paz-García et al., 2012):

$$J_{H^+}^{el} = J_{OH^-}^{el} = \frac{I}{F} \quad (12)$$

Expressions based on these fluxes are typically used to represent boundary conditions in the simulation of EK systems. In case electrode chambers act as reservoirs in which species concentration change with time and flow recirculation may be applied, boundary conditions can be expressed in general form as:

$$\frac{\partial c_i}{\partial t} = (\pm J_i^{Tot} + J_i^{el}) \cdot A/V - Q \cdot c_i/V \quad (13)$$

where J_i^{Tot} and J_i^{el} account for the flux entering/exiting the electrode chamber and the electrolysis reaction, respectively, A is the cross-sectional area of the electrode chamber with volume V , and Q is the recirculation flow.

2.2 Numerical implementation

The proposed NP-Phreeqc-EK model for electrokinetic transport in porous media, based on the Nernst-Planck-Poisson formulation, is implemented by coupling a flow and transport simulator with a geochemical code. Recent studies have taken advantage of the increased flexibility in coupling solute transport and geochemical simulators (Jara et al., 2017; Masi et al., 2017; Jang et al. 2017; Nardi et al., 2014; Rolle et al., 2018; Wissmeier and Barry, 2009), in particular after the release of the modules IPhreeqc (Charlton and Parkhurst, 2011) and PhreeqcRM (Parkhurst and Wissmeier, 2015) facilitating the interface of the geochemical package PHREEQC (Parkhurst and Appelo, 2013) with other software. NP-Phreeqc-EK is based on a COMSOL-PhreeqcRM coupling which allows describing fluid flow, conservative and reactive solute transport, and Coulombic interactions in saturated porous media in presence of an applied electric potential gradient. The description of the ions' displacement is based on a Nernst-Planck-Poisson formulation, accounting for the movement of all charged species in solution instead of selected components. This feature is essential for the evaluation of Coulombic interactions during multicomponent ionic transport as species-dependent parameters and equations affect both the distribution of ions in solution and the electric potential gradient. In NP-Phreeqc-EK a MATLAB LiveLink™ interface is used to manage the sequential-noniterative operator split coupling of COMSOL Multiphysics® 5.3a and PhreeqcRM. The coupling time step is set by the user, possibly as small as possible to minimize errors caused by the operator splitting approach. The internal time steps for the transport and reactive steps are automatically set by COMSOL and PhreeqcRM to

provide the fastest simulation while ensuring convergence within the given tolerances.

The schematic sequence and main features of the NP-Phreeqc-EK simulator are illustrated in Figure 1.

Figure 1. Schematic of the coupling and features implemented in NP-Phreeqc-EK. Green text and background represent PhreeqcRM features whereas the blue color represents the tasks and equations solved in COMSOL.

The transport equations are solved considering the concentrations of the charged species in the system and the electric potential as unknowns. The system of equations is then given by the system of the Nernst-Planck based governing transport equations (Eq. 3) combined with the Poisson's equation (Eq. 6) and the current balance (Eq. 9), which are solved by COMSOL iteratively. At the end of the transport step, concentration values of all species in solution are passed to PHREEQC cells for equilibrium and kinetic geochemical reactions. Such calculations are done by PHREEQC, which can compute homogeneous and heterogeneous equilibria, as well as kinetic reactions with arbitrary rate expressions that are evaluated with an embedded Basic interpreter (Parkhurst and Appelo, 2013). Subsequently, concentration values are passed back to COMSOL for the transport

calculation in the next coupling time step. This procedure is repeated until the end of the reactive transport simulation.

The main features of NP-Phreeqc-EK include:

- multidimensional solution of the fundamental physics governing the displacement of charged species in saturated porous media through a Nernst-Planck-Poisson description;
- charge balance of all ionic species in every point of the domain to comply with the condition of electroneutrality;
- possibility to include multiple flow and transport processes as well as a comprehensive set of kinetic and equilibrium reactions that can be solved in both homogeneous and heterogeneous domains;
- definition of boundary conditions from PhreeqcRM solutions with both constant and time-dependent values and ability to include properties and selected output of the PhreeqcRM calculations directly in COMSOL;
- correction of possible small negative concentration values as a result of numerical instability caused by sharp concentration fronts (Parkhurst and Wissmeier, 2015) with values in each node set the values computed in the previous coupling step (Rolle et al., 2018);
- possibility to store and retrieve the coupling solutions at different time steps.

3. Benchmark problems

The ability of NP-Phreeqc-EK to simulate the transport of charged species for EKR applications is tested for different scenarios with benchmarks involving non-reactive and reactive transport in multidimensional setups. The model is used to solve the Nernst-Planck-Poisson and the charge balance equations described in section 2.1 under the assumption of negligible activity gradients. Figure 2 presents an overview of the different problems selected to validate the code and illustrate its key features.

Figure 2. Schematic representation of the different setups for the validation benchmarks: (a) 3-D cylinder, (b) 2-D domain for migration in concrete, (c) 2-D domain for metal mobilization, (d) experimental setup for EK-ISCO (1-D) and (e) experimental setup for EK-Bio (2-D).

In the first verification test, a comparison with a time-dependent analytical solution shows the ability of the model to simultaneously simulate transient electromigration and

electroosmotic transport. A cylindrical geometry has been considered (Figure 2a) and the system was simulated as simple 1-D setup with an analytical solution, as well as an equivalent fully 3-D system. The 3-D numerical simulations performed with NP-Phreeqc-EK consider four charged species of which two (C^+ and D^-) in the background solution and the other two ions (A^+ and B^-) are present at the anode compartment. The displacement of these charged species is assessed and the magnitude and spatial distribution of the electromigration and diffusive fluxes are compared.

The second verification benchmark considers a 2-D geometry (Figure 2b) and reproduces a rapid migration test for concrete for which a 1-D analytical solution is given by Krabbenhøft and Krabbenhøft (2008). The boundary conditions in the 2-D numerical model are characterized by a limited extension of the electrodes with respect to the total width to highlight the flexibility of NP-Phreeqc-EK to handle asymmetrical configurations. In addition, simulations with and without the condition of electroneutrality are presented, showing the implications in terms of resulting concentration and electric potential gradient distribution.

In the third verification test, a reactive transport simulation has been conducted for the case of metal mobilization due to an acid front generated at the anode. This scenario aims at reproducing mobilization and transport dynamics encountered during electrokinetic remediation of heavy metals in low-permeability media. 2-D numerical simulations performed with NP-Phreeqc-EK are compared with the outcomes of simulations performed with the recently released PHREEQC Ampere (Appelo, 2017) in a 1-D equivalent domain (Figure 2c).

Finally, we consider experimental datasets for the validation from studies investigating the delivery of permanganate (Hodges et al., 2013, Wu et al., 2012b) and nitrate (Gill et al., 2016) for EK-ISCO and EK-Bio applications. The schematic of the two experimental setups is shown in Figure 2d and 2e, respectively. 1-D and 2-D simulations are performed with NP-Phreeqc-EK and the outcomes are compared to the results obtained in the experimental studies.

Table 1 presents an overview of the problems selected to illustrate the proposed EK modeling approach, their key features, the relative benchmark, and the governing equations solved (PDEs describing the EK transport processes and ODEs describing the boundary conditions). The database used in this study is minteq.v4, which considers the Davies equation and the Debye-Hückel equation to calculate the activity coefficients (Parkhurst and Appelo, 2013).

Table 1. Overview of the electrokinetic simulations with NP-Phreeqc-EK and respective benchmarks.

Test	Problem	Description and key features	Benchmark
1	3-D electromigration and electroosmosis	<ul style="list-style-type: none"> - Comparison with analytical solution to assess transport of charged species under external electric potential gradient - Transport of 4 species with same D^{aq} - Differential equations solved: 5 PDEs 	1-D time-dependent analytical solution (Acar et al., 1990)
2	2-D application for ion migration in concrete	<ul style="list-style-type: none"> - Comparison with analytical solution and discussion of the effect of electroneutrality condition - Asymmetrical domain - Transport of 4 species with different D^{aq} - Differential equations solved: 5 PDEs 	1-D steady-state analytical solution (Krabbenhøft and Krabbenhøft, 2008)
3	2-D EK metal mobilization	<ul style="list-style-type: none"> - EK effects on acid front generation at the anode and metal desorption - Aqueous speciation reactions - Surface complexation reactions - Transport of 6 species with different D^{aq} - Differential equations solved: 7 PDEs and 6 ODEs 	1-D simulations with PHREEQC Ampere (Appelo, 2017)

4	1-D EK-ISCO	<ul style="list-style-type: none"> - Comparison of simulated and experimental spatial profiles and breakthrough curve at the anode compartment - Discussion of ionic strength as limiting condition for permanganate delivery - Aqueous speciation reactions - Transport of 4 species with different D^{aq} - Differential equations solved: 5 PDEs and 2 ODEs 	Experimental datasets (Hodges et al., 2013, Wu et al., 2012b)
5	2-D EK-Bio	<ul style="list-style-type: none"> - Comparison of simulated and experimental nitrate concentration profiles - Discussion of the effect of ionic strength as limiting condition for nitrate delivery - Aqueous speciation reactions - Transport of 7 species with different D^{aq} - Differential equations solved: 8 PDEs and 12 ODEs 	Experimental dataset (Gill et al., 2016)

4. Results

4.1 3-D electromigration and electroosmosis

The first benchmark problem considers the simultaneous effect of electromigration and electroosmosis in a cylindrical geometry with length of 0.20 m and radius of 0.02 m, schematically shown in Figure 2a. In the domain, a uniform potential gradient of 100 V/m is applied with the inflow of the species A^+ being displaced from the anode boundary into the domain. The geometrical characteristics and input parameters are listed in Table 2.

Table 2. Input data for the 3-D simulations of electromigration and electroosmosis.

Model geometry and parameters			
Length, L [m]			0.20
Radius, r [m]			0.02
Temperature [K]			298.15
Electric potential gradient [V/m]			100
Electroosmotic permeability, k_{eo} [$\text{m}^2/(\text{V s})$]			2.00×10^{-9}
Tortuosity, τ [-]			0.1
Aqueous diffusion coefficient, D^{aq} [m^2/s]			9.31×10^{-9}
Number of mesh elements			2400
Boundary conditions [mol/m^3]			
	Inflow, $x = 0$ m	Background	Outflow, $x = 0.2$ m
A^+	1	0	Open flux
B^-	1	0	Open flux
C^+	1000	1000	Open flux
D^-	1000	1000	Open flux
Φ [V]	20	-	0

The concentration of the background electrolytes (C^+ and D^-) are 1000 times higher than the concentration of the incoming ions (A^+ and B^-). This ensures a minimum effect of the background solution on the movement of the incoming ions. Therefore, the concentration of the ion A^+ , migrating from the anode to the cathode by electromigration and electroosmosis, can be reproduced by an analytical formulation equivalent to the classic solution of the 1-D advection-diffusion equation (Acar et al., 1990; Ogata and Banks, 1962):

$$c(x, t) = \frac{c_{in}}{2} \left[\text{erfc} \left(\frac{x - k_v t}{2\sqrt{D_i t}} \right) + \exp \left(\frac{k_v x}{D_i} \right) \text{erfc} \left(\frac{x + k_v t}{2\sqrt{D_i t}} \right) \right] \quad (14)$$

where $c(x, t)$ is the concentration in the domain dependent on the space coordinate x and on time t , c_{in} is the concentration at the inflow boundary, and D_i the species' pore diffusion coefficient. The advection term, k_v , accounts for both the electromigration and the electroosmotic fluxes:

$$k_v = -\frac{zF}{RT}D_i\left(\frac{\partial\Phi}{\partial x}\right) - k_{eo}\left(\frac{\partial\Phi}{\partial x}\right) \quad (15)$$

Figure 3a shows the comparison between the 1-D analytical solution and the 3-D numerical model performed with NP-Phreeqc-EK. The agreement between the outcomes of the analytical and numerical models is excellent at the different simulation times. For this problem the main transport mechanisms for the charged ion A^+ is electromigration. This can be appreciated by comparing the three-dimensional maps of the electromigration and diffusive flux components after a simulation time of 6 hours (Figure 3b and 3c). The maps of the flux components show that the electromigration flux is more than one order of magnitude larger than the diffusive flux (Figure 3c), which exhibits higher absolute values in proximity of the advancing front. With the given electric potential gradient, also the electroosmotic flux ($2 \times 10^{-7} \text{ mol}/(\text{m}^2 \cdot \text{s})$) contributes to the displacement of A^+ in the same direction of electromigration, despite being almost twenty times lower than the electromigration component ($3.7 \times 10^{-6} \text{ mol}/(\text{m}^2 \cdot \text{s})$).

Figure 3. (a) Comparison of numerically simulated (lines) concentration profiles of the ionic species A^+ undergoing transport by electromigration, diffusion and electroosmosis with the results of the analytical solution (markers) at different times. (b) 3-D maps of the electromigration flux and (c) the diffusive flux for A^+ after 6 hours.

4.2 2-D application for ion migration in concrete

This benchmark shows the comparison of 2-D simulations with NP-Phreeqc-EK with the 1-D analytical solution of the Nernst-Planck equations combined with the Poisson equation to ensure electroneutrality. The problem is illustrated in Figure 2b, which shows two horizontal electrodes that are displacing four solutes (Na^+ , Cl^- , K^+ , OH^-) in the vertical direction. The extension of the electrodes is limited to half the horizontal length of the domain, creating an asymmetrical distribution of the electric field in the 2-D domain.

The steady-state analytical solution for a 1-D problem has been developed by Krabbenhøft and Krabbenhøft (2008) for both the electric potential field:

$$\Phi(x) = \Phi_0 + \frac{\ln\left(1 + \frac{\Delta c}{c_0} \frac{x}{L}\right)}{\ln(c_L/c_0)} \Delta\Phi \quad (16)$$

where x is the principal direction, L is the length of the domain, Φ_0 and c_0 are the electric potential and the concentration of all cations or anions at the boundary (at $x = 0$), c_L is the concentration of the ions at $x = L$ and $\Delta\Phi$ is the electric potential difference in the domain calculated as $\Delta\Phi = \Phi_L - \Phi_0$ in which Φ_L is the electric potential at $x = L$. The ions' concentration in the domain are expressed by :

$$c_i^\pm(x) = \frac{c_{i,0}^\pm c_L^{\pm\alpha} - c_{i,L}^\pm c_0^{\pm\alpha}}{c_0^\pm c_L^{\pm\alpha} - c_L^\pm c_0^{\pm\alpha}} \left(\frac{x}{L} \Delta c + c_0\right) - \frac{c_{i,0}^\pm c_L - c_{i,L}^\pm c_0}{c_0^\pm c_L^{\pm\alpha} - c_L^\pm c_0^{\pm\alpha}} \left(\frac{x}{L} \Delta c + c_0\right)^{\pm\alpha} \quad (17)$$

where $c_i^\pm$ is the concentration of the species i , $c_{i,0}^\pm$ and $c_{i,L}^\pm$ are the concentration of the species i at the boundary at $x = 0$ and $x = L$, respectively, Δc is the concentration difference of all the cations or anions in the domain calculated as $\Delta c = c_L - c_0$, and $\alpha = k\Delta\Phi/\ln(c_0/c_L)$, with $k = F/(RT)$.

The analytical solution was applied and compared with the outcomes of chloride migration experiments in concrete (e.g., Friedmann et al., 2004, Krabbenhøft and Krabbenhøft, 2008). In this problem, chloride ions, present at a concentration of 500 mol/m³ at the upper boundary, migrate downwards towards the anode where they were initially absent. The electric field responsible for the electromigration of Cl⁻ has an impact also on the displacement and distribution of the other ions in solution (Na⁺, K⁺ and OH⁻). The outcomes of the 2-D numerical simulations performed with NP-Phreeqc-EK are compared with the 1-D analytical solution (Figure 2b) along the left boundary of the domain ($x = 0$ m and $z = [0 - 0.01]$ m). The geometry of the domain and the input parameters are listed in Table 3.

Table 3. Input data for the 2-D model of a migration test for concrete.

Model geometry and parameters				
Length, L [m]				0.01
Width, W [m]				0.05
Temperature [K]				298.15
Inflow boundaries width [m]				0.05
Electric potential boundaries width [m]				0.025
Number of mesh elements				3395
Diffusion coefficients and concentration boundary conditions [mol/m ³]				
	D_i^{aq} [m ² /s]	Inflow, $L=0$ m	Background	Inflow $L=0.01$ m
Na	1.33×10^{-9}	25	25	525
Cl ⁻	2.03×10^{-9}	0	0	500
K ⁺	1.96×10^{-9}	83	83	83
OH ⁻	5.27×10^{-9}	108	108	108
Φ [V]		3	-	0

Figure 4a shows the excellent agreement between the numerical simulations performed with NP-Phreeqc-EK using the Nernst-Planck-Poisson approach (NPPE) and the analytical solution for the different charged species in the domain. OH^- and K^+ are displaced as a result of the Coulombic interactions due to the migration of Na^+ and Cl^- . Numerical simulations were also performed neglecting Coulombic interactions and the electroneutrality condition (Single Species Model, SSM) and their comparison with the analytical solution is shown in Figure 4b. The discrepancy with respect to the results of the analytical solution is apparent since the numerically computed profiles are straight lines and cannot capture the slopes and curvatures predicted by the analytical solution. The use of the Nernst-Planck-Poisson equations is also instrumental to capture the behavior of the electrical potential. Figure 4c shows the perfect agreement of the NPPE simulations with the profile predicted by the analytical solution, showing a variable slope with higher values in the region of low concentrations in proximity of the anode and lower values close to the cathode where the concentrations of the ions are higher. The non-linear behavior of the electric potential cannot be captured neglecting the Coulombic interactions. Figure 4d shows the outcomes of the SSM simulation resulting in a steady-state linear distribution of the electric potential, which differs significantly from the results of the analytical solution. Figure 4e and 4f illustrate 2D maps of the electric potential gradients which also show remarkable differences depending on the chosen transport simulation approach (i.e., considering or neglecting Coulombic interactions).

Figure 4. Comparison of the results of NP-Phreeqc-EK simulations at steady state (lines) with the prediction of the analytical solution (markers). Concentration, electric potential profiles and 2-D maps of the electric potential gradient evaluated considering NPPE (a, c and e) and neglecting Coulombic interactions (b, d and f).

The difference between the NPPE and SSM approaches is also apparent from the computed 2-D steady-state distribution of the ionic species in the domain (Figure 5). The maps show remarkable differences for all ionic species, both in their concentration values and in their spatial distribution patterns.

Figure 5. Spatial distribution of the modeled ions at steady state implementing Nernst-Planck-Poisson equations (NPPE): (a) Na^+ , (c) Cl^- , (e) K^+ and (g) OH^- and without explicit consideration of Coulombic interactions and electroneutrality condition (SSM): (b) Na^+ , (d) Cl^- , (f) K^+ and (h) OH^- .

4.3 2-D EK metal mobilization

A reactive transport scenario has been designed with the aim to simulate the desorption dynamics of a heavy metal by an incoming acid front produced by water electrolysis at the anode. In this case, nickel has been considered as the only heavy metal initially bound to the solid matrix. The equilibrium reactions with the soil matrix include protonation and

deprotonation of the surface and the surface complexation of nickel (Al-Hamdan and Reddy 2005):

The geometrical characteristics of the setup and the chemical composition of the porewater solution in the model are summarized in Table 4.

Table 4. Input data for 2-D EK metal mobilization by generation of an acid front at the anode.

Model geometry and parameters				
Length, L [m]	0.30			
Width, W [m]	0.05			
Temperature [K]	298.15			
Volume, single electrode chamber, V [m ³]	4.00×10 ⁻³			
Cross-sectional area, A [m ²]	0.0133			
Porosity, n [-]	0.60			
Solid density [kg/m ³]	2250			
Tortuosity, τ [-]	0.10			
Number of mesh elements	1500			
Surface properties				
Total number of sites [mol/L solution]	5.62×10 ⁻⁴			
Specific surface area [m ² /g]	24			
Mass of solid for calculation of surface area [g rock/L solution]	1500			
Diffusion coefficients and concentration boundary conditions [mol/m ³]				
	D_i^{aq} [m ² /s]	Inflow, $L=0$ m	Background	Inflow $L = 0.3$ m
H ⁺	9.31×10 ⁻⁹	$\partial c/\partial t = (-J_{H^+}^{Tot} + I/F) \cdot A/V$	1.00×10 ⁻⁴	1.00×10 ⁻⁴
OH ⁻	5.27×10 ⁻⁹	$\partial c/\partial t = -J_{OH^-}^{Tot} \cdot A/V$	1.00×10 ⁻⁴	1.00×10 ⁻⁴
Na ⁺	1.33×10 ⁻⁹	$\partial c/\partial t = -J_{Na^+}^{Tot} \cdot A/V$	10	10
Cl ⁻	2.03×10 ⁻⁹	$\partial c/\partial t = -J_{Cl^-}^{Tot} \cdot A/V$	12	12
Ni ²⁺	6.60×10 ⁻¹⁰	$\partial c/\partial t = -J_{Ni^{2+}}^{Tot} \cdot A/V$	9.9×10 ⁻¹	9.9×10 ⁻¹
NiCl ⁺	1.00×10 ⁻⁹	$\partial c/\partial t = -J_{NiCl^+}^{Tot} \cdot A/V$	2×10 ⁻²	2×10 ⁻²
Φ [V]		30	-	0

At the beginning of the simulation, the composition of the porewater includes mainly Na^+ and Cl^- and nickel is present in equilibrium with the solid matrix at neutral pH in concentration of $9.9 \times 10^{-1} \text{ mol/m}^3$. Applying a constant potential difference at the boundaries of 30 V, an acid front is produced at the anodic chamber. In this example we focus on the acidic front and we assume that the basic conditions generated at the cathode are completely buffered; thus, no alkaline front migrates into the domain. With time, the generated acidic front causes desorption of Ni^{2+} from the surface of the porous medium and its displacement via electromigration towards the cathode. Simultaneously, also speciation reactions occur with formation of NiCl^+ . Figure 6a shows concentration profiles after 80 hours, comparing results from 1-D Phreeqc Ampere (Appelo, 2017) and 2-D NP-Phreeqc-EK. The higher concentration of Cl^- close to the anode boundary with respect to the initial background concentration is a consequence of Coulombic interactions. In particular, as H^+ is produced at the anode by electrolysis, Cl^- migrates towards the anode and accumulates in the adjacent region so that electroneutrality in the solution is ensured.

It is interesting to note that due to the high desorbed Ni^{2+} with a concentration up to approximately 9 mol/m^3 in proximity of the acid front, Na^+ is almost completely displaced from the area where Ni^{2+} has migrated. This is the result of Coulombic interactions that also cause a limited Ni^{2+} concentration being displaced by electromigration beyond the location of the desorption front at $x = 0.075 \text{ m}$. In this region ($x > 0.075 \text{ m}$), the propagation of both H^+ and Ni^{2+} appears to be coupled due to charge interactions, which also determine the displacement of Na^+ .

Figure 6. Comparison between 2-D NP-Phreeqc-EK simulations (lines) and 1-D PHREEQC Ampere solutions (markers) for the case of EK-induced metal desorption after 80 hours: (a) concentration profiles for the major charged species in solution (note that for the ease of visualization $10 \times c_{\text{NiCl}^+}$ concentration is shown), (b) Composition of the surface species, (c) Electrolyte conductivity contribution of each ion ($10 \times \sigma_{\text{NiCl}^+}$), (d) the 2-D map of the electric potential gradient, (e) 2-D visualization of the migration flux, and (f) diffusive flux for Ni^{2+} .

The total desorption of Ni^{2+} from the solid matrix can be observed in Figure 6b which shows the different composition of the surface species. The major part of the system is dominated by SurfONi^+ (1.3×10^{-2} mol/kg) with a smaller fraction of SurfOH^+ (8.5×10^{-4} mol/kg). The surface composition changes significantly after the migration of the acid front. This can be observed close to the left boundary, where SurfONi^+ dropped to values below 1×10^{-7} mol/kg and the dominant surface species becomes SurfOH_2^+ (1.4×10^{-2} mol/kg).

In analogy to Ohm's law, the current density of the system can be approximated as:

$$\mathbf{I} = \sigma_e \nabla \Phi = \left(F^2 \sum_{i=1}^N z_i^2 \frac{nD_i}{RT} c_i \right) \nabla \Phi \quad (21)$$

where σ_e [$\Omega \cdot \text{m}$] is the electrolyte conductivity of the system. Figure 6c shows the contribution to the overall σ_e of each ion, which is in general higher in the zone close to the anode as a result of electrolysis reactions. Consequently, this affects the electric potential distribution in the system and is reflected by lower voltage gradient in the same zone (Figure 6d). Also in this case, electromigration is the main driver of Ni^{2+} displacement after it has entered in solution. Figure 6e shows that the electromigration flux affects the whole concentration of Ni^{2+} and its magnitude in the advancing front (around $4 \times 10^{-6} \text{ mol}/(\text{m}^2 \text{s})$) is more than two orders of magnitude larger than the diffusion component (around $1.5 \times 10^{-8} \text{ mol}/(\text{m}^2 \text{s})$) at the same position (Figure 6f).

4.4 1-D simulation of permanganate delivery

In this benchmark, we considered the experimental setup described by Hodges et al. (2011, 2013) and Wu et al. (2012b) for electrokinetically enhanced transport of permanganate through a clay sample. The setup consists of four compartments, as schematically illustrated in Figure 2d, and includes two electrode chambers separated by two clay cores, the cathode reservoir for the permanganate solution, the clay sample, and the anode reservoir in which the permanganate breakthrough is measured. To avoid interferences caused by electrolysis reactions at the electrodes, the fluid in the electrode reservoirs has been recirculated to maintain a circumneutral pH. At the beginning of the experiment, permanganate (MnO_4^-), initially present as potassium permanganate (KMnO_4), migrates from compartment 3 near the cathode to compartment 2 close to the anode as illustrated in Figure 2d (Hodges et al., 2013).

We consider three different experiments performed in this setup. The first is PI-0, described by Wu et al. (2012b) in which the breakthrough of permanganate transported through the central clay core is measured in reservoir 2. The second and third are PI-1 and PI-2, described by Hodges et al. (2013) which assess the concentration of permanganate at different spatial locations within the central clay core at the end of the experiment. The geometry and parameters used for the simulation of the experiments are listed in Table 5. Reservoir 3 at the inflow ($L=0$ m) is simulated as a closed reservoir in which permanganate accumulates.

Table 5. Input data for 1-D simulations of permanganate delivery in clay.

Model geometry and parameters				
Length PI-0 and PI-2 [m] ^a	0.10			
Length PI-1 [m] ^b	0.18			
Temperature [K]	298.15			
Electroosmotic permeability, k_{eo} [m ² /(V s)] ^b	2.14×10 ⁻⁹			
Tortuosity, τ [-]	0.105			
Volume of single electrode chamber V [m ³]	1×10 ⁻³			
Electrode chamber area A [m ²]	0.0085			
Number of mesh elements	198			
Diffusion coefficients and concentration boundary conditions [mol/m ³]				
	D_i^{aq} [m ² /s]	Inflow, $L=0$ m	Background	Inflow $L=0.3$ m
Na ⁺	1.33×10 ⁻⁹	8.55	8.55	8.55
Cl ⁻	2.03×10 ⁻⁹	8.55	8.55	8.55
K ⁺	1.96×10 ⁻⁹	$\partial c/\partial t = -J_{K^+}^{Tot} \cdot A/V$	0	190
MnO ₄ ^{-a}	2.00×10 ⁻⁹	$\partial c/\partial t = -J_{MnO_4^-}^{Tot} \cdot A/V$	0	190
Φ [PI-0] [V] ^a		2.1	-	0
Φ [PI-1] [V] ^b		11	-	0
Φ [PI-2] [V] ^b		17	-	0

^a Hodges et al., 2013; ^b Wu et al., 2012b.

As shown in Figure 7a, the calibrated model accurately represents the accumulation of MnO₄⁻ in reservoir 2 which starts after 6 days from the beginning of the experiment and proceeds reaching concentrations of 1.5 mol/m³. The simulation results are obtained with the parameters listed in Table 5 that are consistent with the assumptions and parameters of Wu et al. (2012b) who also performed 1-D simulation of EK transport in the same setup. Regarding the distribution of MnO₄⁻ in the domain at the end of the experiments, NP-Phreeqc-EK captures the trends of the observed data for both PI-1 and PI-2 (Figure 7b and 7c, respectively). It is important to note that for both cases, although the concentration at the inlet chamber has been set to 190 mol/m³, the model with the provided input data is able to correctly reproduce the significantly smaller concentrations of MnO₄⁻ that were measured in the domain during the experiments (i.e., close to a value of 8.5 mol/m³).

Figure 7. Measured (markers) and simulated (lines) permanganate concentrations: (a) breakthrough curve at the anode chamber for the experiment PI-0 (Wu et al., 2012b); comparison of spatial profiles for PI-1 (b) and PI-2 (c) (Hodges et al., 2013).

4.5 2-D simulation of nitrate delivery

In this benchmark we consider EK-enhanced nitrate delivery in the experimental setup described by Gill et al. (2015, 2016) and schematically shown in Figure 2e. For this study, two experiments in a permeable porous medium (glass beads) have been selected among the different tests performed by Gill et al. (2016). Nitrate is displaced from the cathode chamber towards the anode chamber by electromigration. Also in this case, electrolysis reactions are buffered to maintain circumneutral pH by the recirculation at constant concentration of HCl at the cathode and by addition of NaOH at the anode. Assuming instantaneous buffer through the water equilibrium, this will result in the net production of Na^+ and Cl^- ions at the anode and at the cathode, respectively. The difference between the two considered experiments is in the nitrate concentration maintained at the cathode chamber: in test HOM-3r1 the concentration is approximately 16 mol/m^3 whereas in test HOM-4 it is 80 mol/m^3 . The boundary conditions of this

problem include constant concentrations of NO_3^- and K^+ at the cathode and time-dependent concentration determined by the recirculation flow in the chamber for the other ions. The anode instead is a closed chamber without recirculation, in which the transported species accumulate and the initial concentrations of NO_3^- and K^+ are zero. At both the electrode chambers, the pH was controlled by addition of HCl and NaOH at cathode and anode respectively. Such amendments neutralize the reactions at the electrodes and results in the release of Cl^- and Na^+ in the system.

Two-dimensional simulations are performed with NP-Phreeqc-EK with the geometric and input parameters listed in Table 6.

Table 6. Input data for 2-D nitrate delivery simulations.

Model geometry and parameters							
Length, L [m]							0.48
Height, H [m]							0.125
Temperature [K]							298.15
Tortuosity, τ [-]							0.15
Recirculation flow at the cathode chamber Q [m ³ /s]							2.5×10^{-8}
Volume of single electrode chamber V [m ³]							2×10^{-3}
Number of mesh elements							300
Diffusion coefficients and concentration boundary conditions [mol/m ³]							
	D_i^{aq} [m ² /s]	Inflow, $L=0$ m		Background		Inflow, $L=0.48$ m	
		HOM-3r1	HOM-4	HOM-3r1	HOM-4	HOM-3r1	HOM-4
Na ⁺	1.33×10^{-9}	$\partial c / \partial t = (-J_{Na^+}^{Tot} + I/F) \cdot A/V$		10.545	14.95	$\partial c / \partial t = J_{Na^+}^{Tot} \cdot A/V - Q \cdot c_{Na^+} / V$	
Cl ⁻	2.03×10^{-9}	$\partial c / \partial t = -J_{Cl^-}^{Tot} \cdot A/V$		8.57	5.15	$\partial c / \partial t = (J_{Cl^-}^{Tot} + I/F) \cdot A/V - Q \cdot c_{Cl^-} / V$	
K ⁺	1.96×10^{-9}	$\partial c / \partial t = -J_{K^+}^{Tot} \cdot A/V$		0	0	16.1	80.6
NO ₃ ⁻	1.90×10^{-9}	$\partial c / \partial t = -J_{NO_3^-}^{Tot} \cdot A/V$		0	0	16.1	80.6
SO ₄ ²⁻	1.07×10^{-9}	$\partial c / \partial t = -J_{SO_4^{2-}}^{Tot} \cdot A/V$		0.97	4.79	$\partial c / \partial t = J_{SO_4^{2-}}^{Tot} \cdot A/V - Q \cdot c_{SO_4^{2-}} / V$	
HSO ₄ ⁻	2.12×10^{-9}	$\partial c / \partial t = -J_{HSO_4^-}^{Tot} \cdot A/V$		7×10^{-6}	2.75×10^{-5}	$\partial c / \partial t = J_{HSO_4^-}^{Tot} \cdot A/V - Q \cdot c_{HSO_4^-} / V$	
NaSO ₄ ⁻	1.38×10^{-9}	$\partial c / \partial t = -J_{NaSO_4^-}^{Tot} \cdot A/V$		0.035	0.22	$\partial c / \partial t = J_{NaSO_4^-}^{Tot} \cdot A/V - Q \cdot c_{NaSO_4^-} / V$	
Φ, $t=0$ h [V]		45	50	-	-	0	0
Φ, $t=144$ h [V]		35.4	38	-	-	0	0

Figure 8 shows the measured and simulated concentration of the major ions in the system

for both configurations at 48, 96 and 144 hours. For both experiments, HOM-3-r1 and HOM-4, the simulated migration of NO_3^- is close to the experimental data measured at the different spatial locations along the porous medium samples. The nitrate front advances with time from the cathode to the anode (from right to left in the plots). This transient behavior is captured well by the numerical simulation. Interestingly, both the experimental data and the outcomes of the simulations show that as NO_3^- advances with time, the concentration of Cl^- locally decreases as a result of Coulombic interactions that tend to maintain an electroneutral solution with the constant concentrations of Na^+ in the

domain. This behavior is particularly evident for HOM-3-r1 after 48 and 96 hours (Figure 8a and 8c). Furthermore, as already observed in the permanganate delivery experiments discussed in the previous section, also in these experiments the maximum concentration of the delivered species (nitrate) in the domain is not strongly dependent on the concentration at the electrode chambers and appears to be limited to considerably smaller values. In particular, the average value of NO_3^- in the domain after 144 hours is 6 mol/m^3 in HOM-3r1 despite a concentration in the cathode chamber of 16.1 mol/m^3 . Similarly, an average concentration of NO_3^- of 17 mol/m^3 has been obtained for HOM-4, although the concentration in the cathode chamber was 80.6 mol/m^3 .

Figure 8. Measured data from Gill et al., 2016 (markers) and results of the NP-Phreeqc-EK simulations (lines) for the major ions at three selected times in experiment HOM-3r1 (a, c and e) and experiment HOM-4 at 48, 96 and 144 h (b, d and f), with indication of the electric potential field over the domain.

5. Discussion

One of the main implications of the Nernst-Planck-Poisson equations is the implicit consideration of Coulombic interactions that affect the coupled distribution of charged species and the intensity of the electric potential to which they are subjected. In the benchmarks presented above this approach has been shown to be of critical importance to accurately reproduce the transport of charged species in EK applications. A feature that we have noted, in particular for the modeling of the experimental setups, is the limitation of the concentration of the incoming species by the background concentration in the porous medium. Such a behavior is clearly visible from the experimental data and is quantitatively confirmed by the Nernst-Planck-Poisson simulations with NP-Phreeqc-EK. This phenomenon has been previously observed and discussed in EK research applied to rapid migration tests for concrete (Krabbenhøft and Krabbenhøft, 2008; Xia and Li, 2013). However, to the best of our knowledge, these limitations have not been extensively discussed for environmental applications of electrokinetic remediation and deserve some attention. The limitation of the concentration of the delivered charged species is a direct consequence of the Poisson's law which defines the charge conservation of electrostatic systems. The main principle is that in a charge-free region such as the bulk water where the electroneutrality condition applies, a net increase of charged ions must always be balanced by the same addition of charged ions of opposite sign. The half-sum of the ions in the background solution can be defined as Γ_s :

$$\Gamma_s = \frac{1}{2} \sum_{i=1}^N |z_i| c_i \quad (22)$$

The main consequence is that during electrokinetic transport a significant change of Γ_s cannot occur as a result of electromigration only, due to the fact that this mechanism displaces positively and negatively charged ions in opposite directions, thus ensuring a stable value of Γ_s . Conversely, advection and diffusion affect positively and negatively charged ions in the same direction with a consequent net increase or decrease of Γ_s .

The influence of Γ_s on the amendment delivery can be observed during the transport of MnO_4^- in Figure 7b and 7c. For both cases, it is observed a maximum concentration in the domain around 8.5 mol/m^3 , value very close to Γ_s (8.55 mol/m^3) despite a concentration of 190 mol/m^3 in reservoir 3 from where permanganate has been delivered. In addition, also the experimental results for nitrate delivery in HOM-3r1 and HOM-4 (Figure 8) support this observation. In particular, the maximum concentration of NO_3^- in the domain for HOM-4 is about 17 mol/m^3 with Γ_s in the order of 20 mol/m^3 and a concentration in the cathode chamber of 80.6 mol/m^3 . These results confirm the presence of a limiting concentration of a charged species that can be delivered in the domain.

Here we propose a simple expression to represent the maximum concentration of a species that is possible to mobilize by electromigration in an electrolyte:

$$c_{i,max} = \frac{c_{i,in} \Gamma_s}{\Gamma_s + c_{i,in}} \quad (23)$$

where $c_{i,max}$ [mol/m^3] is the maximum concentration that a species i , subjected to electromigration from a boundary with concentration $c_{i,in}$ [mol/m^3], can achieve in a domain with a given Γ_s in the background solution.

The proposed relation (Eq. 23), strictly valid for ions with unitary valence and same diffusivity, is compared with experimental data in Figure 9. The values of $c_{i,max}$ and Γ_s have been calculated averaging the measured values in the domain; for the experiments HOM-3r1 and HOM-4 presented by Gill et al. (2016), the concentrations have been chosen after 144 hours. Figure 9a shows four functions obtained with Eq. 23 for different Γ_s for every considered experiment. For reference, the dashed line indicates the linear trend of concentration expected when neglecting Coulombic interactions. The purpose of this representation is to illustrate how the $c_{i,max}$ would change for every experiment as a function of $c_{i,in}$ and Γ_s . The close agreement with the experimental data is indicative of the predictive capabilities of the proposed function that may be used for preliminary estimations. Indeed, when neglecting the assumption of electroneutrality, the expected $c_{i,max}$ would distribute along the 1:1 dashed line, as $c_{i,max}$ would always be equal to $c_{i,in}$. The consequence is that without the explicit consideration of Coulombic interactions, numerical models are not able to provide accurate estimations of $c_{i,max}$ when $c_{i,in} \gg \Gamma_s$.

Figure 9b shows the calculated values of $c_{i,max}$ as a function of $c_{i,in}$, normalized by Γ_s . Notably, as $c_{i,in}/\Gamma_s$ increases, $c_{i,max}$ tends asymptotically to Γ_s .

Figure 9. Experimental values (markers) from Hodges et al. (2013) and Gill et al. (2016) and comparisons with the proposed saturation function (Eq. 23). (a) Predicted and observed values in the domain compared with measurements of permanganate and nitrate for different values of Γ_s observed in the experiments. Solid lines are evaluated using Eq. 23 whereas dashed 1:1 line represents the expected linear trend without considering Coulombic interactions. (b) Comparison with concentrations normalized by Γ_s .

Comparing the proposed relation with experimental data, Figure 9a and 9b show that the expression allows capturing the observed behavior of the experiments performed by Hodges et al. (2013) and Gill et al. (2016) discussed in this study. These observations further highlight the important role of the concentration of the background electrolytes in the porous media when expecting to deliver high concentrations of charged amendments through electromigration and have important implications for practical applications such as EK-ISCO and EK-Bio, since Γ_s plays a key limiting role on the effectiveness of the enhanced delivery.

6. Conclusions

The use of models for electrokinetic remediation is instrumental for the fundamental understanding of the complex flow and reactive transport processes induced by the application of an electric field in subsurface porous media, as well as to improve the design and to optimize EK techniques. In this study, we have proposed and illustrated the capabilities of a new model (NP-Phreeqc-EK) to simulate electrokinetic transport in porous media. The model is a coupling between COMSOL Multiphysics and PhreeqcRM and is based on a multidimensional formulation of the Nernst-Planck-Poisson equations. It allows describing EK flow and transport processes, including electromigration and electroosmosis, the Coulombic interactions between charged species, and a wide range of geochemical reactions. NP-Phreeqc-EK has been validated with analytical, numerical, and experimental results. The model showed the capability to account for the coupled transport of ions with different mobility and to capture the limiting concentration of charged species that is possible to deliver through electromigration. The latter limitation has important practical consequences for EK-based remediation techniques. We have proposed and verified, with experimental outcomes from previous studies, a simple formulation to estimate this limit for amendment delivery based on inflow concentrations and on the ionic composition of the background solution.

We envision future applications of the proposed modeling approach not only in the field of electrokinetic remediation but also for the simulation of EK processes in other fields including in-situ leaching of elements such as metals and metalloids for resource recovery and for sustainable mining activities (Martens et al. 2018). Furthermore, the proposed modeling approach could also be extended to different scales and descriptions

of flow and reactive transport in porous media (Rolle et al. 2013a). For instance, besides the Darcy laboratory scale that was the focus of this study, it could be extended both to the smaller pore scale (De Anna et al. 2014; Rolle and Kitanidis 2014) and to the larger field scale, where physical and geochemical heterogeneity (Cirpka et al., 2012; Fakhreddine et al., 2016; Wen and Li, 2018) will likely play an important role for EK induced transport processes.

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