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Multispecies reactive transport modelling of electrokinetic remediation of harbour sediments

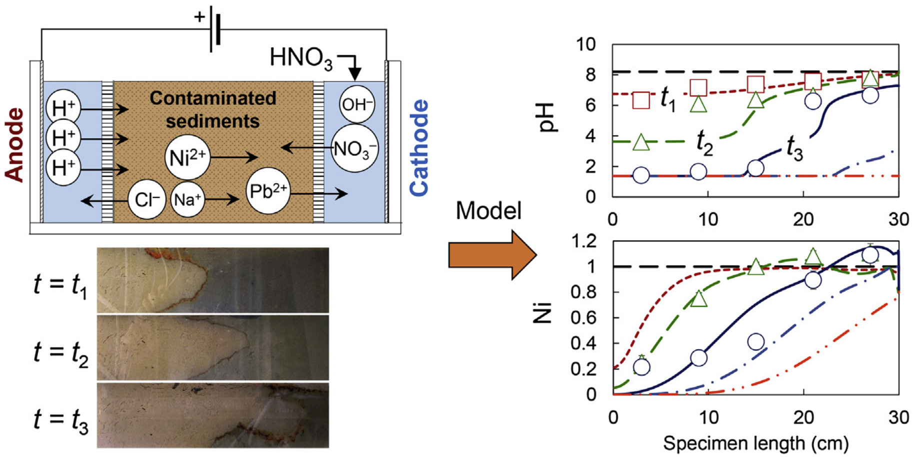
Matteo Masi [a,*], Alessio Ceccarini [b], Renato Iannelli [a]

[a] *Department of Energy, Systems, Territory, and Construction Engineering, University of Pisa, Via C.F. Gabba, 22, 56122 Pisa (PI), Italy*
[b] *Department of Chemistry and Industrial Chemistry, University of Pisa, Via Giuseppe Moruzzi, 13, 56124 Pisa (PI), Italy*

HIGHLIGHTS

- Electrokinetic treatment of marine sediments requires long remediation times.
- Geochemical reactions have strong impact on electrokinetic transport.
- Numerical model describes electrokinetic transport and reactions.
- Model combining mechanistic and empirical approaches can be used for plant design.

GRAPHICAL ABSTRACT



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ABSTRACT

We implemented a numerical model to simulate transport of multiple species and geochemical reactions occurring during electrokinetic remediation of metal-contaminated porous media. The main phenomena described by the model were: (1) species transport by diffusion, electromigration and electroosmosis, (2) pH-dependent buffering of H^+, (3) adsorption of metals onto particle surfaces, (4) aqueous speciation, (5) formation and dissolution of solid precipitates. The model was applied to simulate the electrokinetic extraction of heavy metals (Pb, Zn and Ni) from marine harbour sediments, characterized by a heterogeneous solid matrix, high buffering capacity and aged pollution. A good agreement was found between simulations of pH, electroosmotic flow and experimental results. The predicted residual metal concentrations in the sediment were also close to experimental profiles for all of the investigated metals. Some removal overestimation was observed in the regions close to the anode, possibly due to the significant metal content bound to residual fraction.

1. Introduction

Harbour sediments are frequently polluted by a wide variety of contaminants accumulated during decades of human activities happening in the harbours or transported from upstream sources.

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[*] Corresponding author.
E-mail addresses: m.masi@ing.unipi.it (M. Masi), alessio.ceccarini@unipi.it (A. Ceccarini), r.iannelli@ing.unipi.it (R. Iannelli).

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Electrokinetic remediation (EKR) has been successfully employed for the treatment of sediments with low hydraulic permeability, high salinity and strong acid-neutralizing capacity due to high presence of organics and carbonates [1–6]. This technique relies on applying a low-intensity electric field which mobilizes contaminants and water through the porous medium toward the electrodes due to three main transport mechanisms: electromigration, electroosmosis and electrophoresis. The application of an electric field also induces other complex effects such as pH changes, electrode reactions and geochemical reactions [7]. Moreover, water electrolysis occurring at the electrodes generates hydroxides at the cathode and hydrogen ions at the anode, which are transported by the electric field toward the oppositely charged electrodes, determining acid and alkaline fronts moving in opposite directions. While the acid front is generally favorable for contaminant desorption from the solid matrix, the alkaline front can cause precipitation, thus hindering contaminant transport. To prevent this drawback, chemical reagents (such as weak or strong acids) can be added to the catholyte [8].

In some cases, the effects induced by electric field are not fully understood and their prediction is not achievable merely on an experimental basis. Complexity is mostly due to the high non-linearity and transient geochemistry developing during remediation [9]. Especially in presence of sediments with high buffering and sorption capacity, remediation times of several months can be required to reach the target clean-up levels. In such cases, the prescribed laboratory experiments can get excessively time consuming for the design of full-scale implementations, and modelling could become a necessary tool to assess the main remediation parameters and predict the achievable results.

Several mathematical models have been developed to predict electrokinetic extraction of contaminants [10–18]. Most of them couple the Nernst-Planck equations with auxiliary electrical neutrality equations or with the Poisson equation of electrostatics accounting for the locally induced electrical potential due to the charge unbalance produced when ions migrate with different rates.

However, most of the models developed so far show poor agreement with experimental data. Despite the proper definition of transport processes, several models do not accurately account for species geochemistry and interactions between with the porous material such as adsorption/desorption or precipitation/dissolution, which are indeed key factor for accurate electrokinetic modelling [19]. To overcome these limits, Al-Hamdan and Reddy [20] completed the transport model with a custom subroutine calculating chemical speciation, precipitation-dissolution, oxidation-reduction and adsorption-desorption processes. They overall observed a good agreement with experimental results for cationic metals. However, they used an artificially spiked matrix for model validation, thus neglecting the additional aging effects and heterogeneity occurring in actual contaminated materials.

Mascia et al. [21] also integrated geochemical effects in their model. They represented the interaction with the solid matrix using a two-site geochemical model taking into account ion exchange and surface complexation. They obtained an excellent agreement with validation data, but their calibration and validation were again performed with an artificially spiked matrix (commercial kaolinite clay).

Paz-Garcia et al. [11] developed a generalized model which couples transport processes (electromigration, electroosmosis, diffusion and advection) with a complete geochemical reaction framework (aqueous equilibrium, sorption, precipitation and dissolution). The unsatisfactory field-scale validation suggested that a careful representation of physicochemical processes is needed to predict electrokinetic extraction of contaminants in real situations.

Most models were developed for soils having limited buffering and sorption capacity. Modelling of electrokinetic remediation of high buffering capacity real contaminated marine sediments was not addressed so far. To overcome the limits of previous models and to readily use the model as an analysis and design tool for field scale implementation, we propose a modelling approach combining mechanistic and empirical approaches toward the description of these phenomena.

We present a one-dimensional reactive transport model based on the Nernst-Planck equations coupled with a geochemical model. The model describes species transport driven by diffusion, electromigration and electroosmosis, as well as the effect of surface reactions, precipitation and dissolution, speciation of chemical species and their interaction. To overcome the limited flexibility of current models, the widely validated full geochemical framework PHREEQC [22] was used with least possible number of additional reactions and model parameters. Particular focus was given to sediment buffering capacity to better represent the behavior of real contaminated sediments. After calibration, the numerical model was validated by comparison with experimental data.

2. Materials and methods

2.1. Governing equations

We considered diffusion, electromigration and electroosmosis as the main transport mechanisms. Electrophoresis was neglected, since colloid migration is hindered by the immobile phase of the porous medium [23]. The low hydraulic permeability enabled also to neglect advective flow because of its lower order of magnitude compared to electroosmotic flow. Moreover, we assumed that the porous medium is saturated, isotropic and isothermal; the grains are non-conductive and their surface conductivity is negligible; the osmotic effect related to concentrations gradients and streaming electrical current due to pore water flow are negligible; the pore geometry characteristics (e.g. porosity, tortuosity) do not change over time.

Under these assumptions, the flux density per unit cross-sectional area of porous medium J_i (mol m^{-2} s^{-1}) of a dissolved chemical species i can be expressed as [24]:

$$J_i = -D_i^* \nabla c_i - U_i^* c_i \nabla \phi - k_{eo} c_i \nabla \phi \tag{1}$$

where D_i^* (m^2 s^{-1}) is the effective diffusion coefficient of the i-th specie, c_i (mol m^{-3}) the concentration of the i-th specie, U_i^* (m^2 s^{-1} V^{-1}) the effective ion mobility, ϕ (V) the electric potential and k_{eo} (m^2 V^{-1} s^{-1}) the coefficient of electroosmotic permeability. Due to the tortuous path of ions in the porous matrix, the effective diffusion coefficient and effective ion mobility used in Eq. (1) take into account the effect of porosity n and tortuosity τ [25] and they may be defined as:

$$D_i^* = n\tau D_i \tag{2}$$

$$U_i^* = n\tau U_i \tag{3}$$

where D_i (m^2 s^{-1}) and U_i (m^2 s^{-1} V^{-1}) are the diffusion coefficient and ion mobility at infinite dilution, respectively. The tortuosity factor τ may span in the range 0.01–0.84 [24] depending on characteristics of the porous medium.

Diffusivity and ionic mobility can be related to a single property by the Nernst-Townsend-Einstein relation [24]:

$$U_i^* = \frac{D_i^* z_i F}{RT} \tag{4}$$

where R (8.314 J K^{-1} mol^{-1}) is the universal gas constant, T (K) the absolute temperature and F (96485 C mol^{-1}) the Faraday's constant.