

Reactive-transport modelling of electrokinetic extraction of heavy metals from marine sediments

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Abstracts

This work presents a one-dimensional numerical model to simulate the electrokinetic remediation of real contaminated sediments characterized by a heterogeneous solid matrix and aged heavy metal pollution. The numerical model couples a transport model able to simulate electromigration and electroosmosis with a geochemical model which calculates aqueous speciation, precipitation-dissolution, adsorption and surface complexation reactions. Laboratory scale experiments were carried out to validate the model. We identified the acid buffering capacity as the most significant factor for the extraction of heavy metals from the sediments as their speciation and mobility are strictly dependent on sediment capacity to prevent the pH shift to the acidic range. A good agreement was obtained between simulated pH and metal profiles and experimental data.

1. Introduction

Harbour sediments are frequently affected by a wide variety of pollutants. In most cases, pollution is caused by the contaminant accumulation that lasts for decades due to human activities within the harbours or transported from upstream sources. Remediation of long-term heavy metal contamination is particularly critical, since aging effects cause strong bonds to sediment particles that make pollutant mobilization particularly difficult. Moreover, sediments are often characterized by low-permeability and high acid-neutralizing capacity, due to high presence of fine particles and carbonates [1].

Electrokinetic remediation (EKR) has been successfully applied when these characteristics are met [2]. This technique is based on the application of an electric field which induces the mobilization of contaminants and water through the porous media toward the electrodes, due to three main transport mechanisms: electromigration, electroosmosis and electrophoresis. The electric field also induces a set of complex effects such as pH changes, electrode reactions and geochemical reactions [3]. In presence of sediments with high buffering and sorption capacity, longer remediation times (i.e. months) are required to reach the target clean-up levels. In this case, an extensive laboratory experimentation would be excessively time consuming for the design and practical implementation of this technology at field scale and modelling becomes a necessary tool to identify the main parameters affecting remediation and to predict results.

Several mathematical models have been developed to predict electrokinetic extraction of contaminants from porous media [4–8]. However, numerical modelling of electrokinetic

remediation of high buffering capacity real contaminated marine sediments has not been addressed so far. Most of the models were developed for soils showing limited buffering/sorption capacity or using artificially spiked matrix, in absence of additional aging effects of contaminants occurring in actual contaminated materials.

We implemented a one-dimensional reactive transport model based on the Nernst-Planck equations coupled with a geochemical model. The model describes the contaminant transport driven by chemical and electrical gradients, as well as the effect of aqueous speciation, surface reactions, precipitation and dissolution, adsorption of chemical species and their interaction. Particular focus was given to the role of sediment buffering capacity to improve the description of the behaviour of real contaminated sediments subjected to an electric field. The numerical model was validated by comparison with experimental data.

2. Model Description

2.1. Governing equations

Under an applied electric field, transport of species and water toward the electrodes mainly occurs by diffusion, electromigration and electroosmosis. Electrophoretic transport is not accounted for, due to its limited relevance for the investigated sediments. The mass transport equation (Nernst-Planck) of a dissolved chemical species i can be expressed as:

$$n \frac{\partial c_i}{\partial t} = -\nabla \cdot \left[-D_i^* \nabla c_i - (U_i^* + k_{eo}) c_i \nabla \phi \right] + n R_i \quad (1)$$

where n is the porosity (assumed constant), c_i (mol m⁻³) is the concentration of the i -th species, D_i^* (m² s⁻¹) the effective diffusion coefficient, U_i^* (m² V⁻¹ s⁻¹) the effective ion mobility coefficient, k_{eo} (m² V⁻¹ s⁻¹) the electroosmotic permeability coefficient, ϕ (V) the electrical potential and R_i (mol m⁻³ s⁻¹) is a volumetric net source/sink of the i -th species due to chemical reactions. The effective diffusion and ion mobility coefficients take into account the tortuosity of the porous medium and they are defined as follows:

$$D_i^* = n\tau D_i, \quad U_i^* = n\tau U_i \quad (2)$$

where D_i (m² s⁻¹) and U_i (m² s⁻¹ V⁻¹) are the diffusion coefficient and ion mobility at infinite dilution, respectively and τ is the tortuosity of the porous medium. The diffusivity and ion mobility are related each other by the Nernst-Einstein relation:

$$U_i^* = \frac{D_i^* z_i F}{RT} \quad (3)$$

where R (J K⁻¹ mol⁻¹) is the ideal gas constant, F (C mol⁻¹) is the Faraday's constant, z_i is the ionic charge of the species and T (K) is the temperature.

The electroosmotic permeability k_{eo} is related to the zeta potential ζ (V), dielectric constant ε (F m⁻¹) of the fluid and fluid viscosity η (N s m⁻²) through the following equation [9]:

$$k_{eo} = -\frac{\varepsilon \zeta}{\eta} n\tau \quad (4)$$

Since the zeta potential and the electric field do not remain uniform throughout the specimen during the treatment, we calculated the electroosmotic flow rate by volume-averaging these

quantities. We adopted a generic exponential relationship to compute zeta potential as a function of pH and calibrated the parameters from the data collected during the electrokinetic experiments.

2.2. Chemical reactions

Among the range of reactions that occur when the electric field is applied, we considered only the main phenomena which most experiments recognized as main contributors to the decontamination of saline sediments. In particular the reactions included in the model were: (1) electrolysis of water at the electrodes, (2) pH-dependent adsorption/desorption of H^+ onto the sediment solid matrix, (3) adsorption/desorption of contaminants, (4) aqueous speciation (i.e. formation of complexes), (5) precipitation/dissolution of species. The buffering capacity of the sediments is modelled as a generalized surface complexation reaction. Surface sites are represented by a certain amount of active sites $\equiv SOH$, where S is a metal associated to the solid structure and located at the solid-liquid interface. Depending on electrolyte pH, these groups are subjected to protonation and deprotonation reactions according to the following reactions:



The equilibrium constants for these reactions are:

$$K_1 = \frac{[\equiv SOH_2^+]}{[\equiv SOH][H^+]}, \quad K_2 = \frac{[\equiv SO^-][H^+]}{[\equiv SOH]} \quad (8)$$

K_1 and K_2 were adjusted to fit experimental titration data obtained from batch tests. The results are shown in Figure 1.

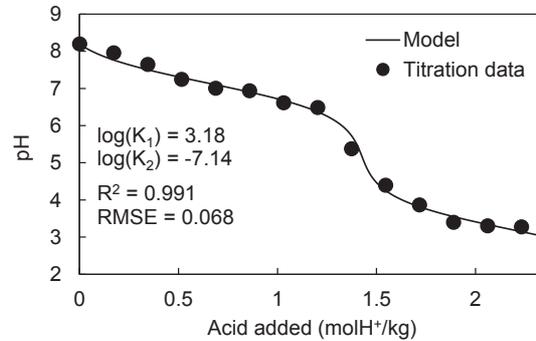


Figure 1. Calibration of the equilibrium constants of the surface complexation model

2.3. Numerical implementation

In the numerical model, under the assumption of local chemical equilibrium, we used a sequential non-iterative split-operator scheme to calculate transport (first step) and reactions (second step) at each time interval. First, the transport of species is computed using a finite-element software (COMSOL) which solves the non-linear system of partial differential equations (Nernst-Planck) for each of the modelled species. Then, reactions are implemented with the USGS PHREEQC

code. The coupling between COMSOL and PHREEQC was done in MATLAB.

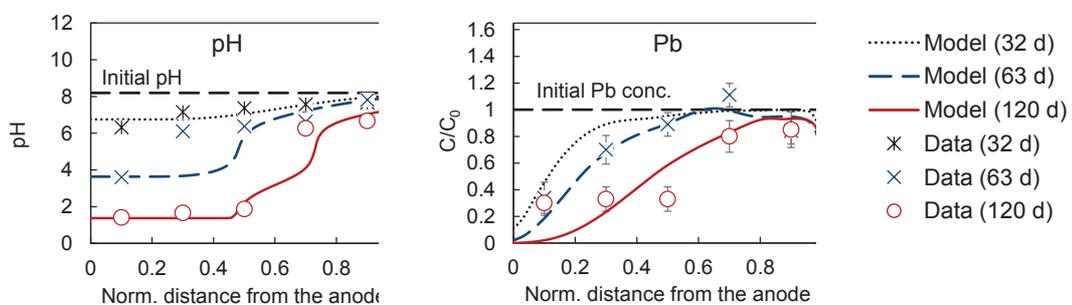
2.4. Experimental setup

The laboratory setup consisted of an acrylic cell with three compartments: a sediment compartment, an anode chamber and a cathode chamber. The sediment compartment size was 30x7x7 cm. Nitric acid was added at the cathode to maintain a constant pH of 3. A constant DC current density of 40 A/m² was applied. Three experiments were run with different treatment durations (32, 63 and 120 days).

3. Results

Three heavy metals were investigated in this study (Pb, Zn, Ni). Along with the targeted contaminants, six major species (H⁺, OH⁻, Na⁺, Cl⁻, NO₃⁻) and the main metal complexes (i.e. PbCl⁺, PbCl₃⁻, PbCl₄²⁻, PbCl₂, PbNO₃⁺, Pb(NO₃)₂, ZnCl⁺, ZnCl₃⁻, ZnCl₄²⁻, ZnCl₂, ZnNO₃⁺, NiCl⁺, NiNO₃⁺) were also included in the model, for a total of 21 components. The simulations were carried out under the following assumptions: constant porosity, saturated porous medium, constant voltage gradient. The diffusion coefficients were derived from literature, the tortuosity factor was set to 0.8, the porosity was experimentally determined (0.35). As initial conditions, initial species concentrations were assumed as being constant in all the domain. The initial pH was 8.2. The voltage at the anode was set to 8 V, according to the values measured during the laboratory experiments.

In Figure 2, model outputs are compared to experimental data obtained in laboratory. Overall, a good agreement between pH profiles and experimental data was observed. However, the position of the acid front was not located accurately, possibly because the pH-buffering process may be kinetically controlled and the effects of neglecting the kinetics are particularly marked for the shorter-term profiles. As for heavy metals, the experimental profiles were reproduced with sufficient accuracy. An overestimation of metal removal was observed in the regions close to the anode. This could be due to metal bonding forms in the sediment. In particular, from sequential extraction we found that the fraction of metals bound to the residual fraction (less mobile fraction) is relevant for the investigated sediment, showing that its role should be taken into account for a further improvement of the model.



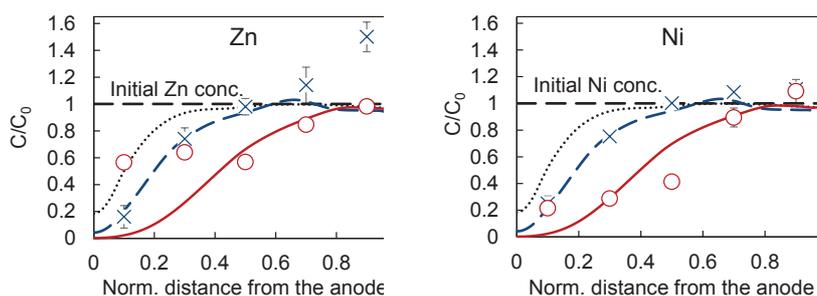


Figure 2. Comparisons between the model and experimental data

5. Conclusions

We developed a reactive transport model which simulates species transport during electrokinetic remediation of marine sediments with high buffering capacity. The model is able to reproduce experimental data with adequate accuracy. Further improvement of the model could be obtained by introducing a kinetic model for proton-induced solid phase dissolution (i.e. dissolution may be kinetically controlled) and by taking into account the metal bonding forms in the sediment.

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