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MODELLING HEAVY METAL TRASPORT AND GEOCHEMICAL EFFECTS DURING MARINE SEDIMENT ELECTROREMEDIATION

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ABSTRACT

We present a numerical model to compute heavy metal transport and geochemical reactions during electrokinetic remediation of contaminated marine sediments. The model describes the contaminant transport driven by chemical and electrical gradients, as well as the effect of surface reactions, speciation of chemical species and their interaction.

In the model we consider only the main phenomena which most experiment recognised as main contributors to the decontamination of saline sediments. The model accounts for: (1) chemical species transport through the porous matrix by electromigration and electroosmosis, (2) induced pH changes, (3) pH-dependent adsorption of H^+ and contaminants onto sediment particle surfaces, (4) aqueous solution speciation (i.e. formation/dissolution of complexes and solid precipitates) and interaction between multiple chemical species. The following simplifications and assumptions were made: constant hydraulic head, saturated porous medium, constant sediment volume and constant voltage gradient. The latter strict condition was verified during laboratory experiments, which showed voltage gradient to be sufficiently stable over the entire duration of the tests.

The model was numerically implemented with a finite element software (COMSOL) and coupled with the PHREEQC USGS code for geochemical equilibrium and surface reaction calculations. A two-step non-iterative sequential scheme was used to calculate transport (first step) and reactions (second step) at each time interval. All chemical and geochemical reactions are assumed to be fast enough to reach their chemical equilibrium at each time interval of the numerical integration.

Model parameters were either derived from literature (tortuosity, diffusion and ion mobility coefficients) or calibrated through laboratory batch tests and bench-scale electrokinetic tests (surface complexation equilibrium constants, porosity). The outputs of the model are the concentration of each considered chemical species during remediation as a function of time and space. Model predictions are finally compared with experimental results.

Keywords: electrokinetic remediation, mathematical model, buffering capacity, PHREEQC, reactive transport

1. Introduction

Harbour sediments are frequently affected by a wide variety of pollutants. In most cases pollution is caused by the accumulation of contaminants 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 (Peng *et al.*, 2009).

Electrokinetic remediation (EKR) is particularly feasible when these characteristics are met (Reddy and Cameselle, 2009). This technique relies on applying a low-intensity electric field

which induces the mobilization of contaminants and water through the porous media toward the electrodes, due to two main transport mechanisms: electromigration (movement of charged ions and molecules), electroosmosis (movement of fluid). The electrophoresis transport is theoretically possible, but usually negligible in the described applications (Acar and Alshawabkeh, 1993).The application of an electric field to the contaminated mass also induces a set of complex effects such as pH changes, electrode reactions and geochemical reactions.

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 these cases, modelling becomes a necessary tool for parameter estimation and result prediction, since laboratory experiments would be excessively time-consuming for practical full-scale implementation of the technology.

A one-dimensional reactive transport model was formulated based on the Nernst-Planck equation coupled with a geochemical model. The numerical implementation of the model was made by coupling PHREEQC-3 USGS code and COMSOL.

COMSOL alone can be used for modelling electrokinetic remediation with the "Transport of diluted species" module, however it offers limited chemical reaction modelling capabilities. Instead, the combined use of PHREEQC and COMSOL can fill this gap. The coupling between COMSOL and PHREEQC in the context of reactive transport modelling was already addressed in literature, e.g. see Wissmeier and Barry (2011) for variably saturated flow simulations and Nardi *et al.* (2014), who developed an interface for using PHREEQC from the COMSOL graphical user interface. These models consider the movement of aqueous "master species" only (i.e. Na, Cl) and not their complexes. This approach works when species are transported by advective flow but under an electrical field different ions move according to their charge and ionic mobility and for a single master specie possibly two or more differently charged aqueous species can exist in solution. Moreover H^+ and OH^- are not master species, so their concentration cannot be defined explicitly in PHREEQC though it is important to correctly represent their individual transport since it determines the sediment pH.

An adapted PHREEQC coupling with an electrokinetic transport model was made by Wu *et al.* (2012) in the PHT3D-EK code. However, this code uses PHREEQC-2 which cannot be suitable for modelling electrolytes with high ionic strength, such as in the case of marine sediments. Conversely, PHREEQC-3 implements additional models which are more suitable for saline environment (e.g. Pitzer model). Moreover, the use of COMSOL for our model provides more flexible modelling capabilities, such as the possibility to add more physics (e.g. unsaturated flow, full Nernst-Planck-Poisson equations, electrode reactions, electrode heat exchange) as well as providing a GUI for easy geometry handling, easy result visualization, parameter optimization and advanced solvers.

2. Model description
2.1. Governing equations
Under an applied electric field, the transport of contaminants and water toward the electrodes occurs by diffusion, electromigration and electroosmosis. Electrophoretic transport is not accounted for, due to its limited relevance for the material under investigation. Moreover, for sediments with low hydraulic permeability, it is possible to assume that the advective flow, i.e. the flow due to pressure gradients, can be neglected because of the lower order of magnitude compared to electroosmotic flow. Therefore, the mass transport equation (Nernst-Planck) for the *i-th* species is given by:

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

where n [-] is the porosity (assumed constant), c_i [mol m^{-3}] is the molar concentration of species i in the pore solution, D_i^* [m^2 s^{-1}] the effective diffusion coefficient, U_i^* [m^2 V^{-1} s^{-1}] the effective ion mobility coefficient, k_{eo} [m^2 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 species due to chemical reactions. The effective diffusion coefficient takes into account the tortuosity of the porous medium and is related to the respective diffusion coefficient in infinitely dilute solution by the following equation (Paz-García *et al.*, 2011):

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

where D_i [m^2 s^{-1}] the diffusion coefficient in solution and τ [-] is the tortuosity of the porous medium. The diffusivity and ion mobility are related by the Nernst-Einstein relation:

$$U_i^* = \frac{D_i^* z_i F}{RT} \tag{3}$$

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.

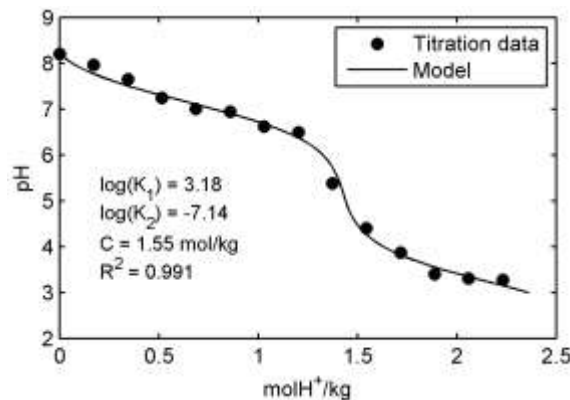## 2.2. Proton complexation model

The acid buffering capacity of the sediment was determined by batch titration tests with HCl. The buffering capacity is modelled as a generalized surface complexation reaction. Surface sites are represented as $\equiv$SOH groups where S is a metal associated to the solid structure (e.g. Al or Si) and located at the solid-liquid interface. Protonation and deprotonation reactions of these groups (Stumm and Morgan, 1995) are represented by:

$$\equiv SOH + H^+ \quad \square \quad \equiv SOH_2^+ \tag{4}$$

$$\equiv SOH \quad \square \quad \equiv SO^- + H^+ \tag{5}$$

The equilibrium constants for these reactions are:

$$K_1 = \frac{[\equiv SOH_2^+]}{[\equiv SOH][H^+]}, \quad K_2 = \frac{[\equiv SO^-][H^+]}{[\equiv SOH]} \tag{6}$$

The complexation model was implemented in PHREEQC and the constants K_1 and K_2 were adjusted to fit experimental titration data by optimization with Nelder-Mead simplex algorithm. The results are shown in Figure 1.

Figure 1: Fitting of surface complexation model to experimental titration data. K_1 and K_2 are equilibrium constants and C [mol kg$_{dry}^{-1}$] is the concentration of surface sites.

2.3. Numerical implementation

In the numerical model, transport processes and chemical reactions are divided into two steps using a non-iterative sequential split operator scheme. First, the transport of species is computed in COMSOL, then reactions are calculated in PHREEQC. The coupling between

COMSOL and PHREEQC was done in the MATLAB environment. We used the iPhreeqc class to call PHREEQC from MATLAB as a COM object.

3. Model verification

To evaluate the model consistency and performance, we performed numerical simulations of electrokinetic remediation of marine sediments contaminated by heavy metals and compared the results to experimental data. Our 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. Deionized water was constantly added at the electrode compartments to avoid excessive accumulation of species at the electrode. A constant DC current density of 40 A/m^2 was applied.

The transport of 6 components (H^+, OH^-, Na^+, Cl^-, NO_3^-, Pb^{2+}) was modelled. The simulations were carried out under the following assumptions: negligible electroosmotic flow, no transport of complexes was considered, constant porosity, saturated porous medium, constant potential gradient. The electroosmotic flow was measured throughout the experiments and it is negligible when using nitric acid. The value of the parameters used for the simulations were: K_1 and K_2 calibrated from titration tests (see §2.2), tortuosity factors derived from literature ($\tau = 1.26$ for cations and $\tau = 1.11$ for anions), diffusion coefficients from literature, 30% porosity.

As initial conditions, initial species concentrations were assumed constant in all the domain. The initial pH was 8.2. The voltage at the anode was set to 8 V, according to the measured values during the laboratory experiments.

The boundary conditions were chosen as follows. At the anode the inward flux of H^+ was calculated with the Faraday's law of electrolysis ($N_{H^+} = I/F$, where N_{H^+} [mol s^{-1}] is the flux of H^+, I [A] the current and F [C mol^{-1}] the Faraday's constant). OH^- value was adjusted to reach equilibrium with H^+ according to $[H^+][OH^-] = 10^{-8}$, with concentrations in [mol m^{-3}]. All the other species concentrations were assumed constant with time to simulate water addition at the electrode compartment. At the cathode, due to the acid addition to maintain pH = 3, H^+ concentration was assumed not to change with time. All the other species were assumed constant as well.

4. Results

The model output was compared to experimental data obtained in laboratory. The results are shown in Figure 2.
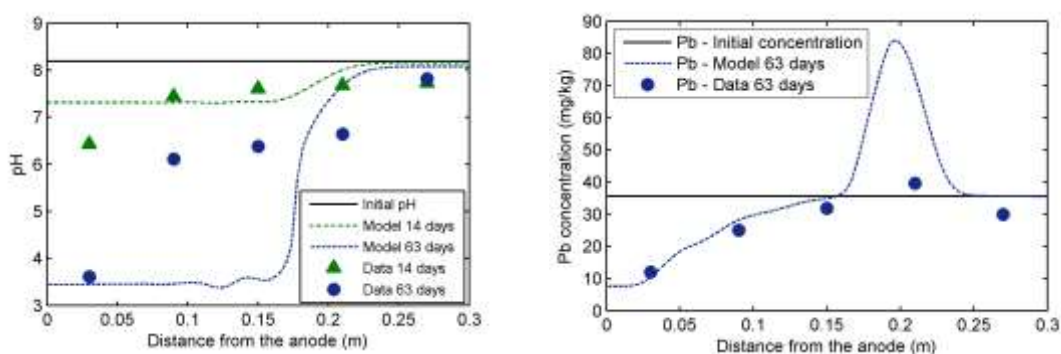
Figure 2: Comparisons between the model and experimental data

Comparisons between the predicted and experimental pH profiles show that the H^+ front advances towards the cathode producing a sharp gradient which is not observed in laboratory. This pH jump can be attributed to the lack of kinetic model for proton complexation (i.e. proton adsorption is not instantaneous).

5. Conclusions

We developed a one-dimensional reactive transport model to simulate species transport during electrokinetic remediation of marine sediments with high buffering capacity. The numerical model couples a transport model able to simulate electromigration of ions and a geochemical model which calculates the aqueous speciation, precipitation-dissolution and surface complexation reactions. The model is able to reproduce the experimental data fairly accurately. The difference between model predictions and the observed data is attributed to the simplifications made (e.g. absence of reaction kinetics, constant voltage gradient, no transport of complexes). The model shows potential applicability as a tool for the design and operation of a real treatment plant.

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