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MIXING ELECTROLYTES DURING ELECTRORECLAMATION OF MARINE SEDIMENT FOR OPTIMIZED REAGENT CONSUMPTION

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ABSTRACT

We studied the effect of catholyte-anolyte mixing during electrokinetic remediation of marine sediment for the optimization of reagent consumption during operation. We developed a model which simulates the effect of recirculation as a function of the flow rate. Laboratory experiments with real dredged sediment were performed in laboratory in order to validate the model.

Reagent consumption is particularly relevant when electrokinetic remediation technique is applied to field scale. A large part of the total cost is covered by reagents for electrolyte conditioning, especially when the buffering capacity of the material subjected to remediation is high, which is a frequent condition for marine sediments due to their high carbonate content. In order to achieve successful removal of contaminants (e.g. heavy metals) it is often necessary to acidify the sediments. Due to the high buffering capacity, longer remediation duration is required and the amount of acid used to reach the target pH can be significantly high.

We performed electrolyte mixing by pumping the anolyte into the catholyte. The anolyte is acid because of the H^+ production at the anode, instead the catholyte tends to become alkaline due to the production of OH^-. In this way the acidity produced at the anode is used directly to buffer the alkalinity at the cathode.

The developed model is composed of a series of continuous flow stirred-tank reactors used to simulate the pH in all the points of the system. To verify the model performance we carried out laboratory experiments at different recirculation flow rates. The model is able to reproduce the experimental data with very good accuracy. Futhermore, the model allowed us to identify the precise behavior of the system. We observed that the acid consumption is reduced even with very low recirculation flow rates. The system response can be divided into a transient state, whose duration depends upon the value of the recirculation flow rate and a steady state which is independent of the flow rate.

We found that the anolyte pH can be maintained to a certain value by making an appropriate choice of the recirculation flow rate. This allows to keep a certain target pH value in the anolyte without further chemical addition.

In conclusion, the experimental and model results allowed to identify specific operating conditions which can be adopted to design of a full scale remediation plant with optimized reagent consumption.

Keywords: electrokinetic remediation, electrolyte recirculation, dredged sediments, full scale plant

1. Introduction
Electroremediation is an emerging technology for in-situ treatment of porous media contaminated by organic and inorganic pollutants (Reddy and Cameselle, 2009). This technique is based on the application of a low-intensity electric field to the contaminated mass to induce the mobilization of contaminants and pore water toward the electrodes, due to electromigration, electroosmosis and electrophoresis (Acar *et al.*, 1995).The applied electric field causes water

electrolysis at the electrodes: H⁺ are produced at the anode and OH⁻ at the cathode respectively. These ions move under the effect of the voltage gradient causing pH changes along the material under treatment. It is essential to adjust the pH of electrolytes and porous material to keep the system performance controlled and avoid undesired effects such as precipitation of carbonates or hydroxides which can hinder the transport processes. This is usually carried out by acid/base addition at the electrode compartments (Yeung and Gu, 2011). Electroremediation of marine sediments presents peculiar drawbacks such as the difficulty in reducing sediment pH due to its high acid neutralization capacity and high pH (Reddy and Ala, 2006). To achieve successful removal of heavy metals it is generally required to lower the pH of the sediment because metals are soluble in the acidic pH range only. This means that longer remediation times are required in order to reach the target clean-up levels because the acid front induced by water electrolysis propagates from the anode to cathode slowly. In full-scale implementation, applied current densities should be low enough to avoid electrolyte overheating and the applied voltage should not be too high to meet safety requirements (Lageman, 1993). For this reason, treatment can last several months, thus requiring accurate operating cost minimization. Together with required electric energy, reagents for pH conditioning can cover a large part of the overall cost for remediation and their consumption should be optimized.

In this paper we studied the effect of mixing the electrolytes during electric field application to marine sediments. This strategy was already investigated in literature, e.g. Cameselle and Reddy (2013) and Lee and Yang (2000). We further studied the electrolyte circulation method by developing a model to calculate the transient and steady state response of an electrokinetic remediation system as a function of recirculation flow rate. The system is modelled as a series of continuous flow stirred-tank reactors (CSTR) which are used to describe the concentration of H⁺ (and thus the pH) at all points of the system. The model validation was carried out by means of laboratory experiments.

2. Laboratory setup

The laboratory experiments were carried out in an acrylic cell (Figure 1), consisting of a sediment compartment, two electrode compartments, an acid reservoir, an anolyte reservoir, two circulation pumps, the power supply and a pH control system.
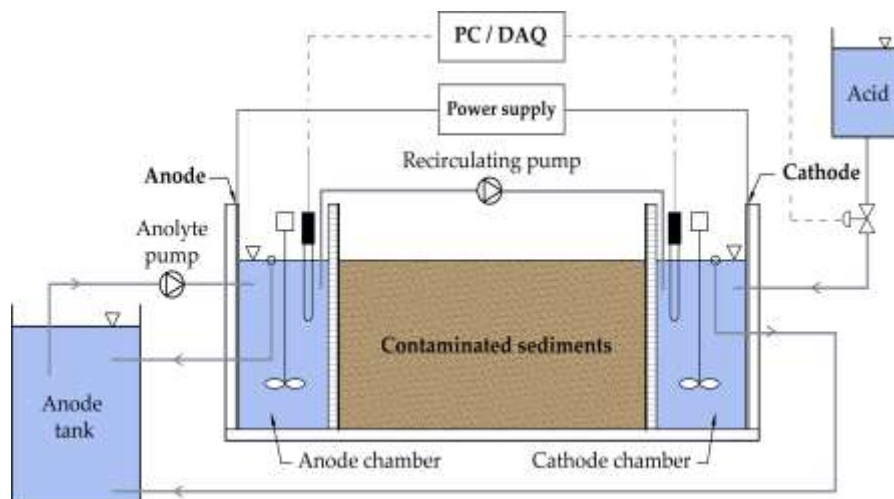

Figure 1: Laboratory experimental setup for electrolyte recirculation tests

3. Model description

The model consists of three interconnected continuous flow stirred-tank reactors (CSTR), used to simulate H⁺ concentration in the anolyte chamber (1), in the catholyte chamber (2) and in the anolyte tank (3), as shown in Figure 2.
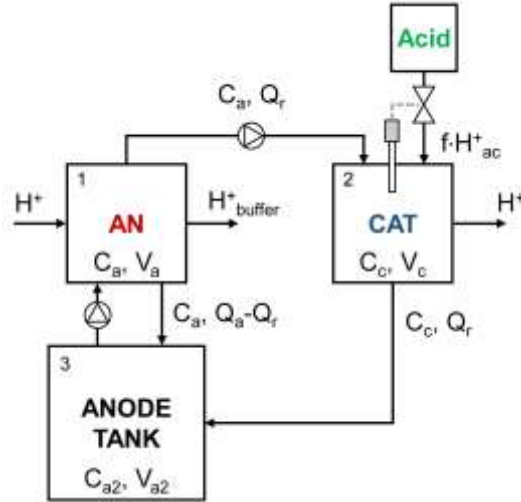
Figure 2: Schematic diagram of the model for simulating electrolyte recirculation

We assumed that all the volumes are constant over time as we neglect: i) the volume of the acid added for pH conditioning, which is many orders of magnitude smaller than the other flow rates, ii) the generation/consumption of water due to electrolysis reactions, iii) water equilibrium reaction and iv) the electroosmotic flow. Therefore, for each reactor i the mass balance for H^+ is:

$$\frac{dC_i}{dt} = \frac{1}{V_i}\left(\sum_j C_j Q_{ji} - \sum_j C_i Q_{ij}\right) + R_i, \quad j \neq i \tag{1}$$

where C_i (mol m^{-3}) is the concentration of H^+ in the reactor i, V_i (m^3) is the volume, Q_{ji} (m^{3}s^{-1}) is the inflow from reactor j to reactor i, Q_{ij} (m^{3}s^{-1}) is the outflow from reactor i to reactor j and R_i (mol s^{-1}) is the rate of generation or consumption of H^+ (including acid addition) in the reactor i.

A valve controls the flow of acid into the catholyte chamber. The valve is opened or closed as a function of catholyte pH. Let t_k be discrete time, the logic associated with the valve is:

$$R_{acid}(t_k) = \begin{cases} 0 & if \quad \mathrm{pH}(t_k) < \mathrm{pH_L} \\ R_{acid}(t_{k-1}) & if \quad \mathrm{pH_L} \leq \mathrm{pH}(t_k) \leq \mathrm{pH_H} \\ f \cdot H^+_{acid} & if \quad \mathrm{pH}(t_k) > \mathrm{pH_H} \end{cases} \tag{2}$$

where $R_{acid}(t_k)$ (mol s^{-1}) is the rate of H^+ moles addition at the instant t_k, $R_{acid}(t_{k-1})$ (mol s^{-1}) is the value at the previous instant, H^+_{acid} (mol s^{-1}) is the constant rate H^+ addition which depends on the acid flow rate and molarity, $\mathrm{pH_H}$ is the relay switch on set-point, $\mathrm{pH_L}$ the switch off set-point and f is the fraction of H^+ added by acid dosage effectively used to buffer OH$^-$ production at the cathode. In the case of nitric acid (HNO$_3$), H^+ reacts with NO$_3^-$ at the cathode, giving ammonium (NH$_4^+$):

$$NO_3^- + 8e^- + 10H^+ \rightarrow NH_4^+ + 3H_2O \tag{3}$$

This means that 8 moles of electrons supplied by the electrical current (which correspond to 8 moles of OH$^-$),cause the consumption of 10 moles of H^+. Hence, the value of f is 0.8.

The whole model is a system of three differential equations (equation 1) which needs three initial condition to be solved, i.e. the initial concentration in the reactors. The system was numerically solved with MATLAB/Simulink using the ode45 (Dormand-Prince) solver with variable time-step size. At the end of the simulation the acid consumption V_{acid} (mol) was computed with the following expression:

$$V_{acid} = \int R_{acid}(t)\, dt \tag{4}$$

4. Results
4.1. Model results

Figure 3 shows the results of model calculation obtained by varying the value of the recirculation flow rate. Even with low flow rates, the acid consumption can be strongly reduced. It can be observed that in all the cases the model reaches a steady state after an initial transient, whose duration depends on the flow rate. The more is the recirculation rate the less is the time required to reach the steady state. After reaching the steady state, the acid consumption remains constant over time and equal to H^+_{buffer} (see Figure 2, left) and the anolyte pH remains fixed to a certain value. The only exception is for 0% recirculation, in which case the anolyte pH always continues to decrease with time.
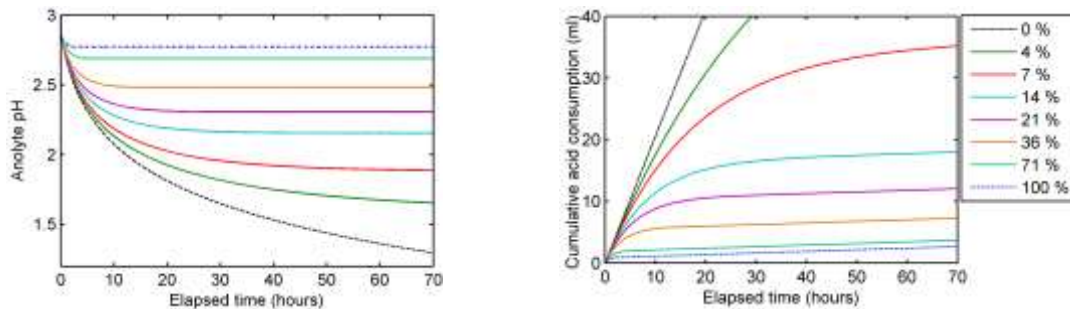

Figure 3: Simulation of anolyte pH (left) and acid consumption (right) at different recirculation flow rates

It is interesting to note that the anolyte pH can be maintained to a certain value by making an appropriate choice of the recirculation flow rate. In the field, the anolyte pH should not decrease too much otherwise the electrolyte circulation apparatus can be damaged by the acidity excess. With this method it is possible to maintain a target anolyte pH without introducing further chemicals in the system such as sodium hydroxide.

4.2. Comparison with experimental data

We carried out four laboratory experiments with different recirculation flow rate values. The set points for catholyte pH control were set to 3.1 and 3. The amount H^+ and OH^- produced at the electrodes were calculated with Faraday's laws of electrolysis. The amount of H^+ transported toward the cathode by electromigration and buffered by the sediment (H^+_{buffer}) is assumed constant with time and this value was calibrated in laboratory. This value is found to be 34.4 ± 5.3 mmol H^+/day. The model output was verified against data from laboratory experiments. Figure 4 shows that there is a very good agreement between the model and data.
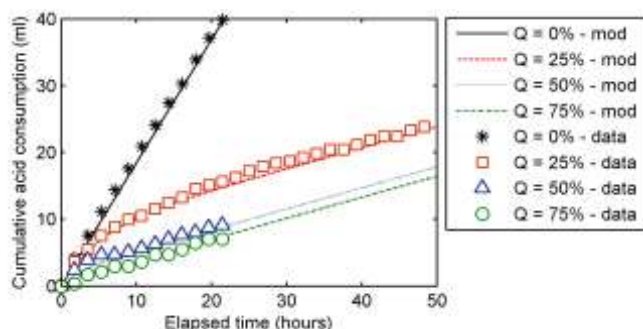

Figure 4: Comparison of model results with experimental data

5. Conclusions

We developed a model for simulating the electrolyte recirculation during electrokinetic remediation of sediments. The model was validated with laboratory scale electrokinetic tests

and the model outputs are in very good agreement with experimental data. The model allowed us to identify specific operating conditions which can be adopted to significantly optimize the operation and costs of a full scale remediation plant.

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