

Influence of chemical reaction kinetics on electrokinetic remediation modelling results

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Abstract

A numerical model describing transport of multiple species and chemical reactions during electrokinetic treatment is presented. The transport mechanisms included in the model were electromigration and electroosmosis. The chemical reactions taken into account were water electrolysis at the electrodes, aqueous species complexation, precipitation, and dissolution.

The model was applied to simulate experimental data from an acid-enhanced electrokinetic treatment of a Pb-contaminated calcareous soil. The kinetics of the main pH buffering process (i.e., calcite dissolution) was taken into account and its time-dependent behavior was described by a rate law. The influence of kinetics was evaluated by comparing the results from a set of simulations in which calcite dissolution was implemented considering thermodynamic equilibrium and another set in which the same reaction was described by the rate law. The results show that the prediction capability of the model significantly improves when the kinetic rate is taken into account.

Keywords: Reactive-transport model, calcite dissolute kinetics, electrokinetic remediation, local chemical equilibrium.

1. Introduction

Most of the physicochemical processes occurring during electrokinetic remediation (EKR) (i.e., the application of electric field for the mobilization of contaminants from soil, sludge, sediment and other matrices) are characterized by dynamic behavior. Understanding the influence of the kinetics of these reactions can significantly help to elucidate the remediation process and to enhance the prediction capabilities of EKR models.

The majority of EKR numerical models have been developed assuming the attainment of chemical equilibrium at each time step of the numerical integration. Reactive-transport models actions are faster equilibrium (LCE) assumption [2], and it has been demonstrated as a suitable approach for modeling reactive-

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transport processes through porous media [3–6]. However, simulation results often displayed certain disagreement with the experimental data, in terms of concentration profiles with excessively sharp gradients compared to those obtained experimentally.

The prediction capability of reactive-transport models could be enhanced by taking into account the kinetics of the chemical reactions. However, in multi-species multi-phase systems, the kinetic laws are very specific and the numerical solution of the system would be unreliable.

The LCE transport models can be enhanced by taking into account the kinetics of the “slow” reactions, namely the heterogeneous reactions (*i.e.*, reactions involving different phases), which are generally characterized by slow kinetic rates [7] compared to aqueous complexation. The rate at which target contaminants are released from their mineral-bound forms is essential in EKR treatments. For example, in acid-enhanced EKR treatments, the acid environment generated at the anode dissolves the contaminant-containing minerals into mobile compounds. The progress of the acid front is generally hindered by the presence of buffering minerals such as, for example, calcite. Experimental results suggested that the dissolution of these carbonates does not take place under equilibrium conditions [8].

In this work, to further develop the prediction capability of EKR models and to understand the role of dissolution kinetics on the rate of extraction of contaminants, the kinetic rates of the calcite dissolution have been taken into account.

2. Materials and methods

The transport of aqueous species and water through porous media, under an applied electric field, is described as a combination of diffusion, electromigration and electroosmosis. Herein, pore fluid advective transport is neglected, due to the low hydraulic permeability of the soils normally treated via EKR. Similarly, electrophoresis has limited relevance in EKR since colloid migration is hindered by the immobile phase of the porous medium [9]. Accordingly, the mass transport equation of the i -th chemical species, based on the Nernst-Planck (NP) equation [10], is described 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, c_i (mol m⁻³) is the concentration, D_i^* (m² s⁻¹) is the effective diffusion coefficient, U_i^* (m² s⁻¹ V⁻¹) is the effective ionic mobility, ϕ (V) is the electric potential, k_{eo} (m² s⁻¹ V⁻¹) is the electroosmotic permeability and R_i (mol m⁻³ s⁻¹) represents a volumetric net source or sink due to chemical reactions.

The effective diffusion coefficient and effective ion mobility in Eq. (1) is defined as

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

where D_i (m² s⁻¹) and U_i (m² s⁻¹ V⁻¹) are, respectively, the diffusion and ion mobility coefficients at infinite dilution and τ the tortuosity.

The Nernst-Townsend-Einstein relation [11] was applied to relate diffusivity to ionic mobility:

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

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

The electric potential ϕ is computed by solving the current conservation equation:

$$\nabla \cdot \mathbf{J} = 0 \quad (4)$$

where \mathbf{J} (A m^{-2}) denotes the current density, described by the Ohm's law, $\mathbf{J} = -\sigma \nabla \phi$, and σ (S m^{-1}) denotes the electrical conductivity, which is related to pore fluid conductivity σ_w (S m^{-1}) by $\sigma = n\tau\sigma_w$. This implies that the solid phase surface conductivity is negligible and that the local electroneutrality condition is fulfilled. The externally-applied current density is a boundary condition for Eq. 4, where the anode represents a current source and the cathode a current sink. The pore fluid conductivity σ_w is calculated by taking into account the conductivity of all the species in the pore solution, while correcting the molal concentration with an electrochemical activity coefficient that is derived from the combination of the Kohlrausch's law and the Debye-Hückel equation [12].

The chemical reactions taken into account were: (1) electrolysis reactions at the electrodes, (2) aqueous phase complexation, and (3) heterogeneous precipitation/dissolution reactions.

As mentioned before, the kinetics of calcite dissolution is included in the model, while all other chemical reactions were still implemented under the LCE assumption. The rate of dissolution of calcite was assumed to follow the general rate law [7,13]:

$$\frac{\partial m}{\partial t} = k \frac{A_0}{V} \left(\frac{m}{m_0} \right)^\alpha \quad (5)$$

where A_0 (m^2) is the initial surface area of the solid particles, V (kg) the mass of solvent, m_0 and m (mol) the amounts of solids at times 0 and t , the exponent α accounts for changes in the specific surface area of the particles during dissolution, and k ($\text{mol m}^{-2} \text{s}^{-1}$) is the specific rate constant, defined as:

$$k = k_f \left[1 - \left(\frac{\text{IAP}}{K_{\text{sp}}} \right)^\beta \right] \quad (6)$$

where k_f is a forward constant, $\text{IAP} = [\text{Ca}^{2+}] [\text{HCO}_3^-]^2 / P_{\text{CO}_2}$ the ion activity product, K_{sp} is the solubility product constant and β is a coefficient related to the stoichiometry of the reaction ($\beta = 2/3$ for calcite).

We considered calcite dissolution as the main buffering process, being generally more abundant than other minerals in calcareous soils. As for all the other heterogeneous reactions, such as dissolution of minerals with heavy metals, existing geochemical studies on kinetic mechanisms are hardly applicable to the conditions developed during EK and specific studies are lacking. Therefore, we did not attempt to model kinetic rates of such reactions. This also helped to prevent excessive increasing of model complexity and keep the number of parameters to a minimum. However, if these slow reactions are still considered as instantaneous (LCE approach), especially when their rates are similar to those of calcite, their apparent rate can be over-predicted by the model. In order to compensate the rate, as a simplified approach, we applied a retardation factor to slow down their speed. This approach is frequently used, e.g., in groundwater modelling studies [14]. We defined the retardation of species in terms of distribution coefficient:

$$S^a = K_d c \quad (7)$$

where S^a (mol kg^{-1}) is the concentration of metal adsorbed onto the solid phase, K_d ($\text{m}^3 \text{kg}^{-1}$) is a linear distribution coefficient between the liquid and solid.

Transport processes and chemical reactions were implemented using a two-steps sequential split-operator scheme [15]. In the first step, the transport equation system (accounting for diffusion, electromigration and electroosmosis and the water electrolysis reactions at the electrode, under electroneutrality conditions) is numerically integrated by means of a finite element method. In the second step, the chemical reactions are calculated. The aqueous formation of complexes, precipitation and dissolution reactions were calculated using the PHREEQC code. For brevity, the reaction equations are not reported here, as they can be found in Parkhurst and Appelo, 1999 [16].

3. Results and discussion

3.1. Simulation of a water-calcite system

In order to evaluate the influence of chemical reaction kinetics on the results of simulations, a simple water-calcite system was modelled. The system consisted of a model calcareous soil composed of an insoluble soil matrix mixed with a certain amount of calcite. Simulations were carried out to represent the behavior of the calcareous soil subjected to acid-enhanced EK remediation.

Preliminary batch simulations were carried out in order to study the sensitivity of the parameter A_0/V of Equation 5, by varying it from $A_0/V = 5$ (bigger particles, slower rate) to $A_0/V = 25$ (smaller particles, faster rate). A value of $\beta = 2/3$ was assumed for the exponent in Equation 5, corresponding to spherical calcite particles.

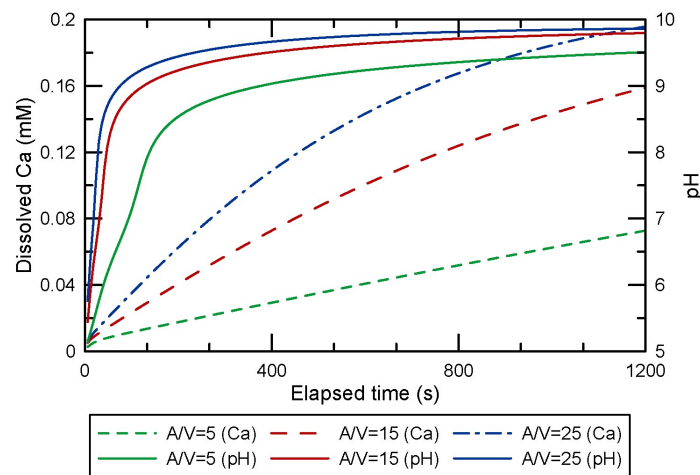


Figure 1. Sensitivity of the parameter A_0/V on the kinetics of calcite dissolution.

Figure 1 shows simulation results on the dissolution kinetics of calcite when putting into contact 1 L aqueous solution (at pH 5 and 1 mM NaCl) and 1 mole of calcite. Equation 5 was integrated in 200 time steps (1200 s each). Both Ca and pH increased with time as the calcite dissolves. The parameter A_0/V governed the rate of dissolution. Higher values of A_0/V (*i.e.*, larger solid surfaces) were responsible for faster dissolution rates.

3.2. Simulation of experimental data

The model developed was applied to simulate the experimental data by Villen-Guzman et al., 2015 [17]. They performed an acid-enhanced EKR treatment of a soil with high content of carbonates and contaminated with a significant amount of lead using acetic acid. The scheme for the acid-enhanced EKR treatment is reported in Figure 2.

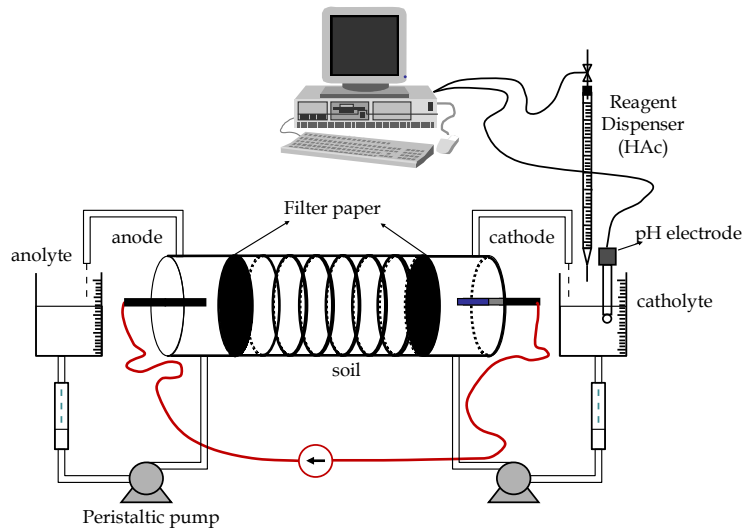


Figure 2. Scheme for an acid-enhanced EKR treatment in horizontal column.

The setup consisted of a horizontal column with 20 cm length and 8 cm diameter. Electrode compartments were well stirred and had a volume of electrolyte of 0.5 L. A constant current density of 20 A/m^2 was applied to the soil. The treatment duration was 15 d. In the cathode compartment was assured with $\text{pH} < 5$ by dropping acetic acid from a burette using an automatic pH-control device.

Paz-Garcia et al, in [18] modeled the mentioned experimental data using the LCE assumption. Their results showed that the presented model represented fairly well the overall reactive transport phenomena. However, the simulation results (see Fig. 3) showed certain disagreement referred to the experimental data with respect to the concentration profiles of Pb, the main contaminant studied, and Ca, indicator of the calcite dissolution.

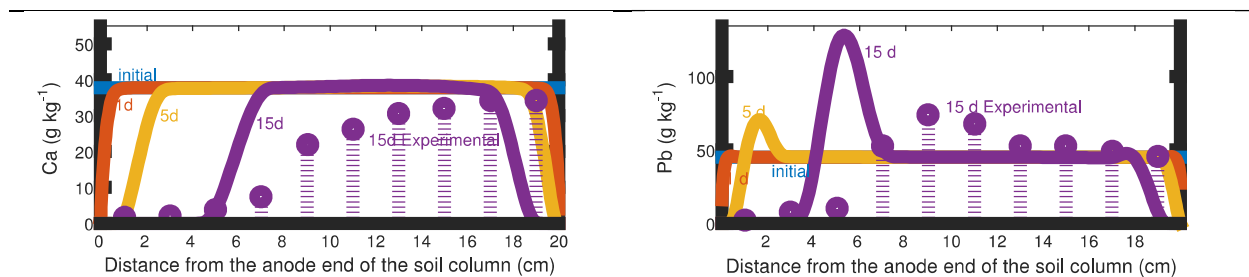


Figure 3. Comparison between the simulation results reported in [18] with the experimental data, from [17]. Figure shows the simulation results for (a) the total amount of Ca (accounting for form CaCO_3 , CaHCO^+ , CaAc^+ , and Ca^{2+}) and (b) the total amount of Pb (accounting for form PbCO_3 , Pb(OH)_2 , PbHCO^+ , PbAc^+ and Pb^{2+}) along the column in 1, 5 and 15 d, as well as the experimental results for 15 d.

Herein, the model has been expanded to include the kinetics of the dissolution of calcite. The dissolution of hydrocerussite (the Pb containing mineral assumed), and the precipitation of lead hydroxide have been assumed fast (compared to calcite) to be included in the LCE module. This is consistent with the results presented in [8]. The model parameters are reported in Table 1.

Table 1. Model parameters.

Parameter	Value	Unit	Description
τ	0.45	-	Tortuosity factor
n	0.49	-	Porosity
T	25	°C	Temperature
$\log(K_{d,Pb})$	3.6	-	Pb distribution coefficient
α	2/3	-	Exponent Equation 5
A_0/V	10	m ² /mol	Specific area of calcite
β	2/3	-	Parameter Equation 6
pH ₀	9.28	-	Initial soil pH

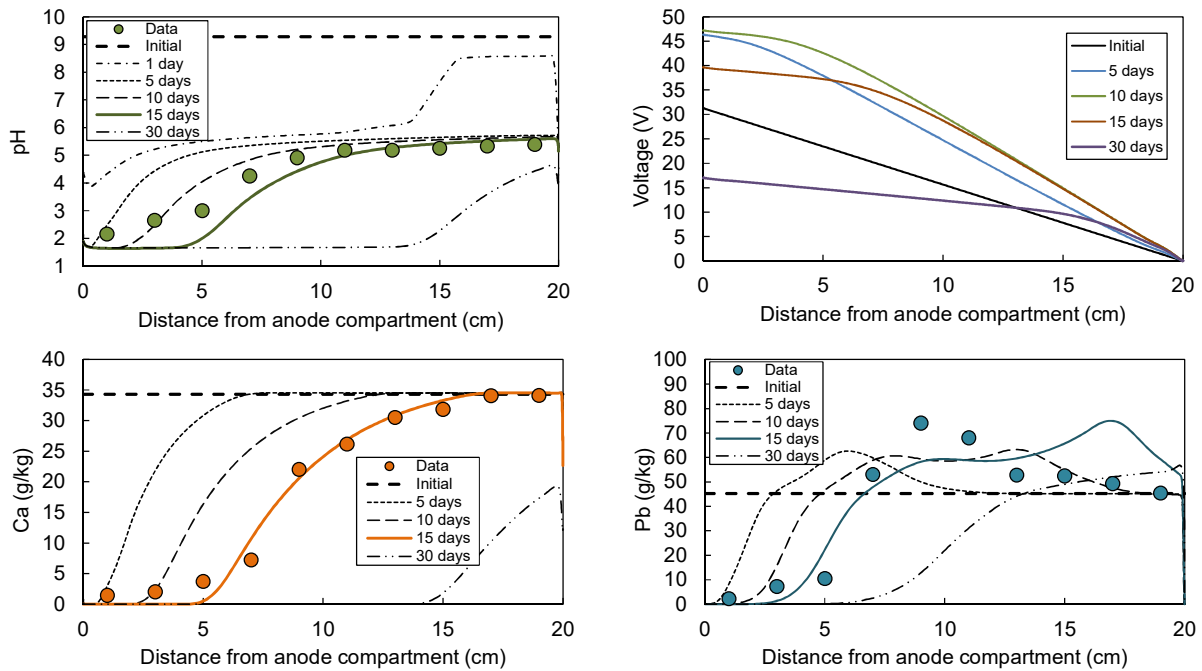


Figure 4. Comparison between the simulation results obtained here and the experimental data from [17]. Figure shows the simulation results for (a) pH, (b) Electric potential, (c) the total amount of Ca (accounting for form CaCO_3 , CaHCO^+ , CaAc^+ , and Ca^{2+}) and (d) the total amount of Pb (accounting for form PbCO_3 , Pb(OH)_2 , PbHCO^+ , PbAc^+ and Pb^{2+}) along the column in 1, 5, 15, and 30 d, as well as the experimental results for 15 d.

The simulation results, presented in Fig. 4, clearly show that including the kinetics of the dissolution of calcite in the numerical model significantly improve the agreement between simulation and experimental results. In particular, it is observed that the acid front entering the soil from the anode penetrates gradually through the soil towards the cathode without sharp almost-vertical gradients, reproducing what was experimentally observed.

4. Conclusions

Herein we have presented a model for electrokinetic remediation of soil, easily adaptable to other porous matrices such as sludge, construction materials or sediments. The model presented here has been enhanced to take into account the kinetics of the chemical reactions that could dominate the overall remediation process. This way, the model presented here can produce better agreement with experimental data than previous models based only on the local chemical equilibrium. The prediction capability of the model is therefore improved.

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References

- [1] J.M. Paz-García, B. Johannesson, L.M. Ottosen, A.B. Ribeiro, J.M. Rodríguez-Maroto, Computing multi-species chemical equilibrium with an algorithm based on the reaction extents, *Comput. Chem. Eng.* 58 (2013) 135–143. doi:10.1016/j.compchemeng.2013.06.013.
- [2] D. Langmuir, *Aqueous Environmental Geochemistry*, Prentice Hall, 1997. <https://books.google.it/books?id=RroPAQAAIAAJ>.
- [3] A. Al-Hamdan, K. Reddy, *Electrokinetic Remediation Modeling Incorporating Geochemical Effects*, *J. Geotech. Geoenvironmental Eng.* 134 (2008) 91–105. doi:10.1061/(ASCE)1090-0241(2008)134:1(91).
- [4] A. Alshawabkeh, Y. Acar, *Electrokinetic Remediation. II: Theoretical Model*, *J. Geotech. Eng.* 122 (1996) 186–196. doi:10.1061/(ASCE)0733-9410(1996)122:3(186).
- [5] S. Amrate, D.E. Akretche, *Modeling EDTA enhanced electrokinetic remediation of lead contaminated soils.*, *Chemosphere.* 60 (2005) 1376–83. doi:10.1016/j.chemosphere.2005.02.021.
- [6] S.-O. Kim, J.-J. Kim, S.-T. Yun, K.-W. Kim, *Numerical and Experimental Studies on Cadmium (II) Transport in Kaolinite Clay under Electrical Fields*, *Water, Air, Soil Pollut.* 150 (2003) 135–162. doi:10.1023/A:1026181800685.
- [7] L.N. Plummer, T.M.L. Wigley, D.L. Parkhurst, *The kinetics of calcite dissolution in CO₂-water systems at 5 degrees to 60 degrees C and 0.0 to 1.0 atm CO₂*, *Am. J. Sci.* 278 (1978) 179–216. doi:10.2475/ajs.278.2.179.
- [8] M. Villén-Guzmán, J.M. Paz-García, G. Amaya-Santos, J.M. Rodríguez-Maroto, C. Vereda-Alonso, C. Gómez-Lahoz, *Effects of the buffering capacity of the soil on the mobilization of heavy metals. Equilibrium and kinetics.*, *Chemosphere.* 131 (2015) 78–84. doi:10.1016/j.chemosphere.2015.02.034.
- [9] J.-W. Yu, I. Neretnieks, *Modelling of transport and reaction processes in a porous medium in an electrical field*, *Chem. Eng. Sci.* 51 (1996) 4355–4368. doi:10.1016/0009-2509(96)00283-7.
- [10] J.M. Paz-García, B. Johannesson, L.M. Ottosen, A.B. Ribeiro, J.M. Rodríguez-Maroto, *Modeling of electrokinetic processes by finite element integration of the Nernst–Planck–Poisson system of equations*, *Sep. Purif. Technol.* 79 (2011) 183–192. doi:10.1016/j.seppur.2011.02.023.
- [11] A.N. Alshawabkeh, Y.B. Acar, *Removal of contaminants from soils by electrokinetics: A theoretical treatise*, *J. Environ. Sci. Heal. . Part A Environ. Sci. Eng. Toxicol.* 27 (1992) 1835–1861.

- doi:10.1080/10934529209375828.
- [12] D.L. Parkhurst, C. a. J. Appelo, Description of Input and Examples for PHREEQC Version 3 — A Computer Program for Speciation , Batch-Reaction , One-Dimensional Transport , and Inverse Geochemical Calculations Chapter 43 of, in: U.S. Geol. Surv. Tech. Methods, B. 6, U.S. Geological Survey (USGS), 2013: p. 497.
- [13] C.A.J. Appelo, D. Postma, Geochemistry, groundwater and pollution, CRC press, 2005.
- [14] M.T. Van Genuchten, P.J. Wierenga, Solute dispersion coefficients and retardation factors, Methods Soil Anal. Part 1—Physical Mineral. Methods. (1986) 1025–1054.
- [15] M. Masi, A. Ceccarini, R. Iannelli, Multispecies reactive transport modelling of electrokinetic remediation of harbour sediments, J. Hazard. Mater. 326 (2017) 187–196. doi:10.1016/j.jhazmat.2016.12.032.
- [16] B.D.L. Parkhurst, C. a J. Appelo, User’s Guide To PHREEQC (version 2) — a Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport and Inverse Geochemical Calculations, 1999. <http://downloads.openchannelsoftware.org/PHREEQC/manual.pdf>.
- [17] M. Villén-Guzmán, J.M. Paz-García, J.M. Rodríguez-Maroto, F. García-Herruzo, G. Amaya-Santos, C. Gómez-Lahoz, et al., Scaling-up the acid-enhanced electrokinetic remediation of a real contaminated soil, Electrochim. Acta. 181 (2015) 139–145. doi:10.1016/j.electacta.2015.02.067.
- [18] J.M. Paz-García, M. Villén-Guzmán, A. García-Rubio, S. Hall, M. Ristinmaa, C. Gómez-Lahoz, A Coupled Reactive-Transport Model for Electrokinetic Remediation, in: A.B. Ribeiro, E.P. Mateus, N. Couto (Eds.), Electrokinet. Across Discip. Cont. SE - 13, Springer International Publishing, 2016: pp. 251–278. doi:10.1007/978-3-319-20179-5_13.