Multiphysics Implementation of Electrokinetic Remediation Models for Natural Soils and Porewaters

López Vizcaíno, R.^a, Yustres, A.^{b,*}, León, M. J.^b, Saez, C.^c, Cañizares, P.^c,

Rodrigo, M.A.^c, Navarro, V.^b

^aDepartment of Chemical Engineering, Institute of Chemical & Environmental Technologies, University of Castilla-La Mancha, Campus Universitario s/n, 13071 Ciudad Real, Spain

^bGeoenvironmental Group, Civil Engineering School, University of Castilla-La Mancha, Avda. Camilo José Cela s/n, 13071 Ciudad Real, Spain

^cDepartment of Chemical Engineering, Faculty of Chemical Sciences&Technologies, University of Castilla-La Mancha, Campus Universitario s/n, 13071 Ciudad Real, Spain

*** Corresponding author:** angel.yustres@uclm.es, Civil Engineering School, University of Castilla-La Mancha, Avda. Camilo José Cela s/n, 13071 Ciudad Real, Spain

GRAPHICAL ABSTRACT

ABSTRACT

Models of electrokinetic soil remediation systems have been developed significantly in recent decades. A wide range of physicochemical phenomena occurs in this type of process, which makes it difficult to capture all of the system's complexity in a model. Therefore, existing models do not attempt to simulate the behaviour of the entire geochemical system of natural soils and their porewaters but rather focus on the pollutant compounds of interest. This paper proposes a conceptual and numerical model that includes geochemical speciation other than the phenomena that have been described by other authors. In addition, a comparative modelling exercise is performed with a composition of natural porewater and a simplified equivalent composition. The results show that the buffering system of carbonates affects the temporal evolution and spatial distribution of the pH. Because the pH controls many of the phenomena that occur during this type of remediation, simulations using realistic geochemical systems are critical.

KEYWORDS:

Electrokinetic soil remediation, Multiphysics simulation, geochemical modelling, unsaturated soil

1. INTRODUCTION

Electrokinetic remediation (EKR) is a technology that has recently been applied in soil decontamination processes [1, 2]. EKR technology allows contaminants of different ionic natures to be mobilised via various transport mechanisms that are generated by applying a low-intensity electric field between electrodes installed in the contaminated soil. This effect has generated significant interest in EKR technology in the field of in-situ soil decontamination. In addition, the energy requirements are generally low and can be supplied by renewable energy-based systems that are easily installed in any area to be decontaminated [3-5].

Electro-osmosis and electromigration are the main forms of mass transport that take place in the soil during an EKR process. The process of electro-osmosis causes the movement of water in the Debye layer, which is located along the surfaces of the soil particles. Generally, the soil surface charge is usually negative, so water that is capable of being mobilised through this mechanism has high concentrations of positive counter ions, and electro-osmotic transport is generally directed towards cathodes [6-8]. Through the process of electromigration, it is possible to mobilise various ionic species present in the porewater that are electrically attracted to the oppositely charged electrodes. Among these ionic species are protons and hydroxyl ions generated in the electrochemical reactions of water electrolysis:

which occur on the surfaces of the anodes (Eq. 1) and cathodes (Eq. 2). The movement of these species produces an acidic pH front towards the cathodic electrodes and a basic pH front towards the anodic electrodes, whose velocity, in addition to the

electromigration process, is significantly influenced by advective/diffusive processes and the soil's buffering capacity [9-11]. The pH fronts form a pronounced pH gradient in the soil that can favour the precipitation/solubilisation of species, adsorption processes, and ionic exchange between the soil and the porewater and, importantly, influence the chemical speciation of substances in the medium.

The coupling of these phenomena makes the design, analysis, and implementation of an EKR process in contaminated soil a very complex task. The development of mathematical models is necessary to characterise the interactions of the many physical, chemical, and electrochemical processes that occur simultaneously and therefore facilitate making predictions about the scaling of the technology. For this reason, the development of mathematical models of EKR processes has been important over the last 25 years. Shapiro et al. [7] and Shapiro and Probstein [8] developed a one-dimensional mathematical model that considered the chemical equilibria of substances in the porewater, electrochemical reactions, diffusive and electro-osmotic transport, and ionic electromigration. The model was developed for the decontamination of a synthetic soil (kaolin) spiked with acetic acid and phenol. This model was improved by adding coupling complexation, adsorption and precipitation/dissolution processes by Jacobs et al. [12] and extended to a two-dimensional domain by Jacobs and Probstein [13]. Other authors [14-16] developed a one-dimensional theoretical model that was applied to remove lead spiked in a mixture of kaolinite and sand, for which they estimated the pH profiles generated in the soil. Mascia et al. [17] proposed a similar model for the removal of cadmium. These models were generalised by Paz-Garcia et al. [9] for application to soils contaminated with many metals. Other authors [18, 19] have developed two-dimensional models that focused on the electrokinetic removal of metals and its application, in particular, to the remediation of soils contaminated with copper. Ribeiro et. al. [20] developed a model adapted for the

removal of organic pollutants and used atrazine as an example. A three-dimensional model has also been developed and used to simulate the electrokinetic transport of ions in soils under unsaturated conditions assuming that the lines of the electrical current in a soil during the application of an electrical gradient are analogous to the lines of a water current generated under a hydraulic gradient [21, 22].

In this context, as proposed by Al-Hamdan & Reddy [23], many previous models utilise simplified geochemical systems because they generally contain fewer than 10 species, taking into account the reactants and products of the chemical and electrochemical reactions that can occur. This implies that the chemical speciation generated in the EKR process is quite limited and cannot faithfully reproduce the behaviour observed in real applications, where the composition of the natural porewater can be very complex. As mentioned above, chemical speciation is strongly related to the pH of the medium, which determines the extent to which many physico-chemical processes that directly affect the efficacy of an EKR process can be developed.

This study developed a model, M4EKR (Multiphysics for ElectroKinetic Remediation), that is applicable to electrokinetic remediation processes in natural unsaturated soils for the removal of ionic species present in porewater. An extended geochemical system with 34 species that are involved in 24 chemical equilibria resulting from the presence of the most common major ions in many natural groundwaters was studied. The model includes the transport of species due to electro-osmosis, electromigration, diffusion and advective flow.

After describing the proposed formulation, the scope of the model is illustrated by simulating an EKR process of a natural soil and porewater as opposed to the synthetic saturating waters that have been proposed in other studies. The results show the descriptive capacity of the proposed model. Finally, the same process is analysed

assuming a reduced geochemical model. This exercise illustrates the limitations of simplified models that do not allow several relevant processes that occur in natural porewaters to be simulated. The results confirm the convenience of using extended geochemical models to improve the characterisation and design of EKR processes in soils under natural conditions.

2. CONCEPTUAL AND NUMERICAL MODEL

The proposed model is a model of the reactive transport of solutes in partially saturated soils subjected to an external electrical gradient. For conceptual simplification, isothermal conditions (298.15 K over the entire domain) are assumed, and the gas pressure (GP) remains constant and equal to atmospheric pressure

2.1. Water transport

The balance of the mass of water per unit volume in a porous medium is given by the expression:

$$\frac{\partial m_w}{\partial t} + \nabla \cdot \mathbf{l}_w = 0 \quad (3)$$

where $\nabla \cdot$ is the divergence operator, $\mathbf{l}_w$ is the mass flow of water ($\text{kg m}^{-2} \text{s}^{-1}$), and m_w is the mass of water per unit total volume (kg m^{-3}), which is defined as:

$$m_w = \phi \cdot Sr \cdot \rho_w \quad (4)$$

where ϕ is the porosity, ρ_w is the water density, and Sr is the degree of saturation of the soil. Sr is modelled using van Genuchten's retention curve [24], which is defined via the expression:

$$Sr = \left(1 + (\alpha_{VG} \cdot s)^{n_{VG}} \right)^{-m_{VG}} \quad (5)$$

where α_{VG} , n_{VG} and m_{VG} are fitting parameters, and s is the matric suction, which is given by the difference between the gas pressure and liquid pressure, $P_G - P_L$.

The mass flow of water is defined by the sum of the hydraulic flux contributions ($\mathbf{l}_w^h$), which are estimated via Darcy's law, and the electro-osmotic flux ($\mathbf{l}_w^{eo}$), which is defined by the semi-empirical Helmholtz-Smoluchowski formulation [25]. Therefore, in the proposed model, we have:

$$\mathbf{l}_w = \mathbf{l}_w^h + \mathbf{l}_w^{eo} = \rho_w \cdot (\mathbf{q}_w^h + \mathbf{q}_w^{eo}) = \rho_w \cdot \mathbf{q}_w \quad (6)$$

$$\mathbf{q}_w^h = -K_e^h \cdot (\nabla P_L + g \cdot \rho_w \cdot \nabla z) \quad (7)$$

$$K_e^h = K_{sat}^h \cdot k_{rel}^h = K_{sat}^h \cdot Sr^3 \quad (8)$$

$$\mathbf{q}_w^{eo} = -K_e^{eo} \cdot \nabla E = -K_{sat}^{eo} \cdot Sr^3 \cdot \nabla E \quad (9)$$

where K_e^h is the effective hydraulic permeability of the soil, which is calculated by multiplying the saturated permeability (K_{sat}^h) by a relative permeability function. A Brooks and Corey-type power function was chosen for the relative permeability [26] with an exponent of 3. In addition, ∇ is the gradient differential operator, g is gravity, z is the vertical coordinate, E is the electric potential, K_e^{eo} is the effective electro-osmotic permeability of the soil, which is calculated using the same formulation employed in the calculation of K_e^h , and K_{sat}^{eo} is the saturated electro-osmotic permeability.

2.2. Chemical species transport

The proposed geochemical system includes a total of N species generated from the combination of M components selected among the species [27]. $M-2$ equilibrium equations of the total mass of each component are defined (one for each except for Cl^- ,

which is obtained by electroneutrality, and for H₂O, which was proposed in Eq. 3), generically formulated as:

$$\frac{\partial m_m}{\partial t} + \nabla \cdot \mathbf{l}_m = R_m \quad (10)$$

where m_m is the total mass of component m per unit total volume (mol m⁻³), $\mathbf{l}_m$ is the total molar flux of component m (mol m⁻² s⁻¹), and R_m is the rate of production or consumption of component m (mol m⁻³ s⁻¹). The parameter m_m is defined as:

$$m_m = \phi \cdot Sr \cdot \rho_w \cdot C_m \quad (11)$$

where C_m is the total molal concentration of component m (mol kg_w⁻¹).

Several transport mechanisms of species through the soil occur in EKR processes, so $\mathbf{l}_m$ will be the sum of each of the contributions associated with the involved mechanisms, including advective flow generated by the hydraulic gradient ($\mathbf{l}_m^h$) and the electrical gradient ($\mathbf{l}_m^{\text{eo}}$), electromigratory flow ($\mathbf{l}_m^{\text{em}}$) and diffusive-dispersive flow ($\mathbf{l}_m^{\text{dif}}$):

$$\mathbf{l}_m = \mathbf{l}_m^h + \mathbf{l}_m^{\text{eo}} + \mathbf{l}_m^{\text{em}} + \mathbf{l}_m^{\text{dif}} \quad (12)$$

where each of these mass flows is defined as:

$$\mathbf{l}_m^h = \mathbf{l}_w^h \cdot C_m \quad (13)$$

$$\mathbf{l}_m^{\text{eo}} = \mathbf{l}_w^{\text{eo}} \cdot C_m \quad (14)$$

$$\mathbf{l}_m^{\text{em}} = \rho_w \cdot \sum_{i=1}^N \alpha_i^m \cdot c_i \cdot \mathbf{q}_i^{\text{em}} \quad (15)$$

$$\mathbf{l}_m^{\text{dif}} = -\rho_w \cdot \sum_{i=1}^N D_i \cdot \alpha_i^m \cdot \nabla c_i \quad (16)$$

where α_i^m is the molar contribution to the total concentration of component m of species i (see Section 2.5), and c_i is the molal concentration of the species. In addition, $\mathbf{q}_i^{\text{em}}$ is the migration velocity, which is defined via the expression:

$$\mathbf{q}_i^{\text{em}} = -\mu_i^{\text{e}} \cdot \nabla E \quad (17)$$

where μ_i^{e} is the effective ionic mobility characteristic of species i and is defined via the expression proposed by Mattson et al.[21]:

$$\mu_i^{\text{e}} = \phi \cdot Sr \cdot \tau \cdot \gamma_i \cdot \mu_i^{\text{o}} \quad (18)$$

where, γ_i is the coefficient of activity of species i (see Section 2.5), μ_i^{o} is its ionic mobility at infinite dilution in water ($\text{m}^2\text{V}^{-1}\text{s}^{-1}$), and τ is the tortuosity of the medium. Some authors have proposed different empirical models [28] that link the volumetric soil water content ($\phi \cdot Sr$) and the tortuosity factor using, among others, power functions. These formulations can resemble the power function dependence on the degree of saturation that it is used in the expression of the relative permeability (Eqs. 8 and 9). However, these empirical models are neither valid for all kind of soils nor for all ionic species. Consequently, for the sake of simplicity, a unique and constant value of tortuosity is considered in the present work since the main objective of the model is to understand the fundamental physical-chemical phenomena during an EKR process.

The effective diffusion coefficient of each species, D_i^{e} , is estimated via the expression:

$$D_i^{\text{e}} = \phi \cdot Sr \cdot \tau \cdot D_i^{\text{o}} \quad (19)$$

where D_i^{o} is the binary diffusion coefficient in water (m^2s^{-1}). The effective diffusion/dispersion coefficient D_i for one-dimensional flow is estimated via [29]:

$$D_i = D_i^e + \delta_i^L \cdot \left| \mathbf{q}_i^{\text{em}} + \mathbf{q}_w^{\text{h}} + \mathbf{q}_w^{\text{eo}} \right| \quad (20)$$

where δ_i^L is the longitudinal dispersivity coefficient (m).

Because it is easier to find values of the binary diffusion coefficient than values of the ionic mobility at infinite dilution in the literature, μ_i^0 is estimated by means of D_i^0 via the Nernst-Einstein equation [30]:

$$\mu_i^0 = \frac{D_i^0 \cdot z_i \cdot F}{R \cdot T} \quad (21)$$

where z_i is the charge number of species i , F (C mol^{-1}) and R ($\text{J mol}^{-1} \text{K}^{-1}$) are the Faraday and ideal gas constants, respectively, and T is the temperature (K), which, as discussed previously, is assumed to be constant.

The generation or consumption of the total mass of any component in the soil does not occur in any case, so R_m is zero in the M -2 balance equations. The only electrochemical reactions are the electrolysis of water, and they take place in electrolyte wells.

2.3. Transport of electric charge

The distribution of the electrical potential in the system must satisfy the equilibrium equation of the total electric charge:

$$\frac{\partial Q}{\partial t} + \nabla \cdot \mathbf{i} = R_Q \quad (22)$$

where Q is the total electric charge (C m^{-3}), R_Q is the rate of generation/consumption of the electric charge ($\text{C m}^{-3} \text{s}^{-1}$), and $\mathbf{i}$ is the total current density (A m^{-2}), which is calculated by applying Ohm's law, formulated generically as:

$$\mathbf{i} = -\sigma_a \cdot \nabla E \quad (23)$$

where σ_a is the apparent electrical conductivity obtained via the formulation defined by Rhoades [31]. In it, the soil is assumed to be a system in which electrical current can follow three different conducting paths: (1) exclusively through the liquid phase, (2) exclusively through the surface of the solid phase, and (3) through a combination of these elements. The conductivity of the solid phase, σ_s , is estimated by the empirical relationship presented by Rhoades in Friedman [32]:

$$\sigma_s = 0.023 \cdot \%_{\text{clay}} - 0.0209 \quad (24)$$

where σ_s is defined in dS m^{-1} , and $\%_{\text{clay}}$ is the weight percentage of the clay soil particles considered. In addition, the conductivity of the aqueous phase in the pores, σ_w , is assumed to be constant and is estimated via [33]:

$$\sigma_w = \sum_{i=1}^N (\lambda_{o,i} \cdot \gamma_i \cdot c_i) \quad (25)$$

$$\lambda_{o,i} = \frac{\rho_w \cdot D_i^0 \cdot z_i^2 \cdot F^2}{R \cdot T} \quad (26)$$

where $\lambda_{o,i}$ is the ionic molal conductivity of species i . Given the condition of electroneutrality throughout the system and assuming that no charge accumulation capacity is present during the EKR process, it is assumed that $\partial Q / \partial t = 0$ at all times [13].

Therefore, the electric charge equilibrium is reduced to solving the expression:

$$\nabla \cdot \mathbf{i} = 0 \quad (27)$$

2.4. Mass balance in electrolyte wells.

Figure 1 shows a conceptual model of the configuration of the electrodes and electrolyte wells in the model.

Figure 1. Conceptual model of the one dimensional domain proposed for simulation.

This configuration was chosen because it allows a strictly one-dimensional configuration that facilitates the system model. Additionally, to determine the evolution of the mass of the M -2 components in both electrolyte wells, the wells were considered ideal continuous stirred tank reactors, and M -2 additional mass balance equations were formulated for each well, which have the following common expression for both the anode and the cathode:

$$\frac{\partial M_m^*}{\partial t} = \dot{M}_m^{\text{in},*} - \dot{M}_m^{\text{out},*} + R_m^* \quad (28)$$

where the $*$ superscript is equal to A for the anode and C for the cathode, M_m corresponds to the total mass of component m (mol), $\dot{M}_m$ is the mass input rate (superscript *in*) or mass output rate (superscript *out*) in the well of component m (mol s^{-1}), and R_m is the rate of production or consumption of the component (mol s^{-1}), which is calculated via Faraday's law for those components that have electrochemical reactions. Consequently, we have:

$$M_m^A = \rho_w \cdot V^A \cdot C_m^A \quad (29)$$

$$\dot{M}_m^{\text{in} A} = \rho_w \cdot C_m^{\text{o} A} \cdot \int_{\partial\Omega} (-\mathbf{q}_w \cdot \mathbf{n}) \cdot dS^A \quad (30)$$

$$\dot{M}_m^{\text{outA}} = \int_{\partial\Omega} (-\mathbf{l}_m \cdot \mathbf{n}) \cdot dS^A \quad (31)$$

$$\dot{M}_m^{\text{inA}} = \rho_w \cdot C_m^{\text{oA}} \cdot \int_{\partial\Omega} (-\mathbf{q}_w \cdot \mathbf{n}) \cdot dS^A \quad (32)$$

and at the cathodic well:

$$M_m^C = \rho_w \cdot V^C \cdot C_m^C \quad (33)$$

$$\dot{M}_m^{\text{inC}} = \int_{\partial\Omega} (\mathbf{l}_m \cdot \mathbf{n}) \cdot dS^C \quad (34)$$

$$\dot{M}_m^{\text{outC}} = \rho_w \cdot C_m^C \cdot \int_{\partial\Omega} (\mathbf{q}_w \cdot \mathbf{n}) \cdot dS^C \quad (35)$$

$$R_m^C = \frac{\varphi_m^C}{F} \cdot \int_{\partial\Omega} (-\mathbf{i} \cdot \mathbf{n}) \cdot dS^C \quad (36)$$

where V is the volume of the electrolyte in the well (m^3), S is the active electrode surface (m^2), C_m^A and C_m^C are the total molal concentrations of component m in the anolyte and catholyte, respectively, C_m^o is the total initial molal concentration, $\mathbf{n}$ is the vector normal to the surface of the contact between the soil and the electrolyte well, and φ_m is the ratio between the number of moles of component m generated electrochemically and the number of moles of electrons exchanged in the redox half reaction. This study considers the redox reactions related to water electrolysis, which generate H^+ at the anode via Eq. 1 and OH^- at the cathode via Eq. 2; therefore, $\varphi_{\text{H}^+}^A = \varphi_{\text{OH}^-}^C = 1$.

2.5. Chemical speciation equations.

The calculation of chemical speciation is based on solving a system of M nonlinear equations of the type:

$$C_m - C_m^{\text{cal}} = 0 \quad (37)$$

where the concentrations C_m are the variables of state of the equilibrium equations described above, and C_m^{cal} is calculated via the expression:

$$C_m^{\text{cal}} = \sum_{i=1}^N \alpha_i^m \cdot c_i = \sum_{i=1}^N \alpha_i^m \cdot \frac{a_i}{\gamma_i} \quad (38)$$

where α_i^m is the molar contribution of species i to component m . This contribution is equal to the stoichiometry coefficient of component m in the formation reaction of species i and is positive if m is a reactant and negative if m is a product of the production reaction of species i . For example, in the water dissociation reaction, H_2O and H^+ are the components, and OH^- is the species obtained from their combination; therefore, $\alpha_{\text{OH}^-}^{\text{H}_2\text{O}} = 1$ and $\alpha_{\text{OH}^-}^{\text{H}^+} = -1$.

The activity of each species i , a_i , is calculated via the generic chemical equilibrium equation:

$$\log(a_i) = \log(K_i^{\text{eq}}) + \sum_{m=1}^M (\alpha_i^m \cdot \log(a_m)) \quad (39)$$

where K_i^{eq} is the equilibrium constant of the formation reaction of i . Moreover, γ_i is the coefficient of activity that corresponds to each species i , which is estimated via the WATEQ Debye Hückel formulation [34].

For chemical speciation, three additional equations are necessary to calculate the water activity ($a_{\text{H}_2\text{O}}^{\text{cal}}$), the concentration of free chlorine ions ($c_{\text{Cl}^-}^{\text{cal}}$) and the ionic strength (I^{cal}):

$$\log(a_{\text{H}_2\text{O}}) - \log(a_{\text{H}_2\text{O}}^{\text{cal}}) = 0 \quad (40)$$

$$c_{\text{Cl}^-} - c_{\text{Cl}^-}^{\text{cal}} = 0 \quad (41)$$

$$I - I^{cal} = 0 \quad (42)$$

where the activity of water ($a_{H_2O}^{cal}$) is obtained via the Garrels and Christ formulation [35]:

$$a_{H_2O}^{cal} = 1 - 0.017 \cdot \sum_{i=1}^{N-H_2O} c_i \quad (43)$$

The activity of the free chlorine ion ($a_{Cl^-}^{cal}$) is calculated by applying the electroneutrality principle:

$$a_{Cl^-}^{cal} = \gamma_{Cl^-} \cdot c_{Cl^-}^{cal} = - \frac{\gamma_{Cl^-}}{z_{Cl^-}} \cdot \sum_{i=1}^{N-Cl^-} z_i \cdot c_i \quad (44)$$

Finally, I^{cal} is obtained via:

$$I^{cal} = \frac{1}{2} \cdot \sum_{i=1}^N z_i^2 \cdot c_i \quad (45)$$

The variables a_m , $a_{H_2O}^{cal}$, c_{Cl^-} and I are the unknowns of the system of algebraic equations that must be solved to obtain the speciation of the porewater.

2.6. Numerical implementation

The M4EKR model was implemented in Comsol Multiphysics [36], which is a partial differential equation solver based on the application of the finite element method with Lagrange multipliers. The "multiphysics" capability was used without the pre-programmed modules provided by the software. Thus, both differential and algebraic equations to be solved were defined using constitutive models to consider the initial conditions and the boundary conditions imposed. This was possible due to the versatility and adaptability of this type of program based on a multiphysics environment [37-39]. In addition, the automatic differentiation techniques [40] included in some programs, such as Comsol Multiphysics, provide symbolic expressions to define the iteration matrix [41],

which improves the convergence behaviour of the model and allows the complexity of the problem to increase while maintaining solution efficiency[42, 43]. Thus, in the proposed extended geochemical model, we defined 9 partial differential equations (mass balance in the soil), 16 ordinary differential equations (mass balance in the electrolyte wells), and 11 algebraic equations (chemical speciation), which yields a total of 36 state variables to be solved in each time step. In the simplified model, 4 partial differential equations, 4 ordinary differential equations and 11 algebraic equations were solved to yield 18 state variables.

3. SIMULATION OF EKR PROCESS

3.1. Modelled configuration.

An EKR process of a natural soil from an area near a clay quarry in Spain was studied. According to the Unified Soil Classification System, the soil is a low plasticity clay (CL), whilst according to the texture classification of the United States Department of Agriculture (USDA), it is a silty loam [44]. Table 1 shows the mineralogical and textural parameters of the material. A natural density of 1.89 g/cm^3 and a gravimetric water content of 32.8% were assumed to reproduce realistic compaction conditions [44]. Under these compaction conditions, it was reasonable to hypothesise that the soil deformability is negligible. The hydraulic behaviour was characterised by oedometric tests and by the use of a chilled-mirror psychrometer [45] to obtain the retention curve. Table 2 shows the obtained parameters.

Table 1. Textural and mineralogical of modeled soil.

Size fraction	Mass percentage (%)
Sand	26.9
Silt	68.2
Clay	4.9
Mineral	Mass percentage (%)
Quartz	7
Feldspar	15
Calcite	4
Kaolinite	26
Smectite	28
Illite	20

Table 2. Soil hydraulic parameters.

Parameters	Values	Units
α_{VG}	0.0147	kPa ⁻¹
n_{VG}	1.2593	-
m_{VG}	0.2059	-
ϕ	0.4681	-
K_{sat}^h	2.03×10^{-10}	m s ⁻¹
K_{sat}^{eo}	2.4×10^{-9}	m ² V ⁻¹ s ⁻¹
ρ_s	2681.5	kg m ⁻³
δ_i^L	0.01	m
τ	1.00	-

Figure 2 shows the dimensions of the experimental setup. The electrokinetic reactor is composed of a $15 \times 15 \times 3$ cm central compartment that houses the soil to be treated and two side compartments with dimensions of $15 \times 3 \times 3$ cm that are used as electrolyte wells, in which the electrodes are located. The electrodes have a prismatic geometry with an electrochemically active surface equal to the well/soil interface ($S^A=S^C=45$ cm²). The

electrolyte volume in the wells is assumed to be constant throughout the simulation process ($V^A=V^C=135\text{ cm}^3$).

Figure 2. Dimensions and boundary conditions of the modeled system.

Table 3 shows the M components and N species that make up the two geochemical models, including the extended geochemical model (EGM) and the simplified geochemical model (SGM). The equilibrium reactions, their thermodynamic constants [46] and the physicochemical properties of each species are also shown. The values of the binary diffusion coefficients in water of each species were not found in the literature, so they were estimated using the expression of Pikal [47].

Table 3. Thermodynamical properties of the modelled geochemical systems.**EGM components:** Cl⁻, H₂O, H⁺, CO₃⁻², SO₄⁻², NH₄⁺, Ca⁺², Mg⁺², Na⁺ and K⁺.**SGM components:** Cl⁻, H₂O, H⁺, Na⁺.

Species	Reactions	log K_i^{eq} (25°C)	Hard core diameter / Å	D_i^0 / m ² s ⁻¹	Used in the geochemical model
Cl ⁻	Cl ⁻	0	3.6	2.03×10 ⁻⁹	EGM/SGM
H ₂ O	H ₂ O	0	3.4	5.27×10 ⁻⁹	EGM/SGM
H ⁺	H ⁺	0	4.1	9.31×10 ⁻⁹	EGM/SGM
CO ₃ ⁻²	CO ₃ ⁻²	0	4.7	9.55×10 ⁻¹⁰	EGM
SO ₄ ⁻²	SO ₄ ⁻²	0	4.7	1.07×10 ⁻⁹	EGM
NH ₄ ⁺	NH ₄ ⁺	0	4.1	1.98×10 ⁻⁹	EGM
Ca ⁺²	Ca ⁺²	0	5.7	7.93×10 ⁻¹⁰	EGM
Mg ⁺²	Mg ⁺²	0	5.7	7.05×10 ⁻¹⁰	EGM
Na ⁺	Na ⁺	0	4.1	1.33×10 ⁻⁹	EGM/SGM
K ⁺	K ⁺	0	4.1	1.96×10 ⁻⁹	EGM
OH ⁻	H ₂ O ↔ OH ⁻ + H ⁺	-14	3.6	5.27×10 ⁻⁹	EGM/SGM
HCO ₃ ⁻	CO ₃ ⁻² + H ⁺ ↔ HCO ₃ ⁻	10.33	3.6	1.18×10 ⁻⁹	EGM
H ₂ CO ₃ [*]	CO ₃ ⁻² + 2H ⁺ ↔ H ₂ CO ₃ [*]	16.68	3.4	1.92×10 ⁻⁹	EGM
HSO ₄ ⁻	SO ₄ ⁻² + H ⁺ ↔ HSO ₄ ⁻	1.98	3.6	1.33×10 ⁻⁹	EGM
NH ₃	NH ₄ ⁺ ↔ NH ₃ + H ⁺	-9.23	3.4	2.00×10 ⁻⁹	EGM
CaHCO ₃ ⁺	Ca ⁺² + CO ₃ ⁻² + H ⁺ ↔ CaHCO ₃ ⁺	11.43	4.1	5.06×10 ⁻¹⁰	EGM
CaCO ₃	Ca ⁺² + CO ₃ ⁻² ↔ CaCO ₃	3.22	3.4	4.46×10 ⁻¹⁰	EGM
CaSO ₄	Ca ⁺² + SO ₄ ⁻² ↔ CaSO ₄	2.31	3.4	4.71×10 ⁻¹⁰	EGM
Ca(OH) ⁺	Ca ⁺² + H ₂ O ↔ Ca(OH) ⁺ + H ⁺	-12.78	4.1	2.13×10 ^{-10*}	EGM
MgHCO ₃ ⁺	Mg ⁺² + H ⁺ + CO ₃ ⁻² ↔ MgHCO ₃ ⁺	11.37	4.1	4.78×10 ⁻¹⁰	EGM
MgCO ₃	Mg ⁺² + CO ₃ ⁻² ↔ MgCO ₃	2.98	3.4	4.21×10 ⁻¹⁰	EGM
MgSO ₄	Mg ⁺² + SO ₄ ⁻² ↔ MgSO ₄	2.23	3.4	4.45×10 ⁻¹⁰	EGM
Mg(OH) ⁺	Mg ⁺² + H ₂ O ↔ Mg(OH) ⁺ + H ⁺	-11.68	4.1	2.13×10 ^{-10*}	EGM
NaHCO ₃	Na ⁺ + HCO ₃ ⁻ ↔ NaHCO ₃	10.08	3.4	6.73×10 ⁻¹⁰	EGM
NaCO ₃ ⁻	Na ⁺ + CO ₃ ⁻² ↔ NaCO ₃ ⁻	1.27	3.6	5.85×10 ⁻¹⁰	EGM
NaSO ₄ ⁻	Na ⁺ + SO ₄ ⁻² ↔ NaSO ₄ ⁻	0.94	3.6	6.18×10 ⁻¹⁰	EGM
NaOH	Na ⁺ + H ₂ O ↔ NaOH + H ⁺	-14.75	3.4	1.89×10 ^{-10*}	EGM/SGM
KSO ₄ ⁻	K ⁺ + SO ₄ ⁻² ↔ KSO ₄ ⁻	0.88	3.6	7.46×10 ⁻¹⁰	EGM
KOH	K ⁺ + H ₂ O ↔ KOH + H ⁺	-14.46	3.4	1.89×10 ^{-10*}	EGM
MgCl ⁺	Mg ⁺² + Cl ⁻ ↔ MgCl ⁺	0.35	4.1	2.13×10 ^{-10*}	EGM
CaCl ⁺	Ca ⁺² + Cl ⁻ ↔ CaCl ⁺	-0.29	4.1	2.13×10 ^{-10*}	EGM
KCl	K ⁺ + Cl ⁻ ↔ KCl	-0.5	3.4	1.89×10 ^{-10*}	EGM
NaCl	Na ⁺ + Cl ⁻ ↔ NaCl	-0.5	3.4	1.89×10 ^{-10*}	EGM/SGM
CaCl ₂	Ca ⁺² + 2 Cl ⁻ ↔ CaCl ₂	-0.64	3.4	7.54×10 ⁻¹⁰	EGM

* Obtained by using Pikal's model [46]

Table 4 shows the initial conditions of the problems simulated in this study. The compositions of the electrolyte and porewater used in the EGM were defined from a local sample of groundwater with a significant carbonate concentration [48]. Two criteria were followed to determine the analogous composition employed in the SGM simulation: the same initial pH (7.6) and the same concentration of positive charges in the initial state. Figure 2 shows the boundary conditions applied in the simulations.

Table 4. Initial conditions.

Total Concentration*			Chemical Speciation			Hydraulic			Electrical		
molal	EGM	SGM	molal	EGM	SGM	kPa	EGM	SGM	V	EGM	SGM
C_{H^+}	3.04×10^{-3}	-4.18×10^{-7}	a_{H^+}	2.51×10^{-8}	2.51×10^{-8}	P_L	100	100	E	1	1
$C_{CO_3^{2-}}$	2.93×10^{-3}	0	$a_{CO_3^{2-}}$	4.41×10^{-6}	0						
$C_{SO_4^{2-}}$	1.13×10^{-3}	0	$a_{SO_4^{2-}}$	5.25×10^{-4}	0						
$C_{NH_4^+}$	2.77×10^{-6}	0	$a_{NH_4^+}$	2.39×10^{-6}	0						
$C_{Ca^{+2}}$	2.30×10^{-3}	0	$a_{Ca^{+2}}$	1.29×10^{-3}	0						
$C_{Mg^{+2}}$	2.06×10^{-3}	0	$a_{Mg^{+2}}$	1.17×10^{-3}	0						
C_{Na^+}	3.58×10^{-3}	1.17×10^{-2}	a_{Na^+}	3.13×10^{-3}	1.05×10^{-2}						
C_{K^+}	5.31×10^{-5}	0	a_{K^+}	4.65×10^{-5}	0						
			a_{H_2O}	9.99×10^{-1}	9.99×10^{-1}						
			c_{Cl^-}	7.24×10^{-3}	1.17×10^{-2}						
			I	1.66×10^{-2}	1.17×10^{-2}						

*Concentration of liquid pore and electrolytes (anolyte and catholyte)

3.2. EGM simulation

To assess the scope of the M4EKR model, the EKR process was simulated with the EGM described in Section 2 for a total test time of 3 days. Figure 3 shows the spatial distribution of a set of variables of interest for different times.

Figure 3. Spatial distribution in the EGM at selected times of (a) pH ; (b) total normalised concentration of the CO_3^{2-} component; (c) total normalised concentration of the SO_4^{2-} component; (d) total normalised concentration of the Na^+ component; (e) total normalised concentration of the K^+ component; (f) total normalised concentration of the Ca^{2+} component; (g) total normalised concentration of the Mg^{2+} component; (h) Ionic strength, I .

The pH distribution follows the typical pattern described in the literature [14, 23], including an acidic front and a basic front that move towards the centre of the domain from the anodic and cathodic wells, respectively (Figure 3a). Both are located in a central

position (although closer to the cathode due to the higher ionic mobility of H^+), and the resulting front moves slowly to the position of the cathode well. The behaviours of different ions are similar to what is expected theoretically (Figures 3b to 3g). Thus, increased concentrations of the anionic and cationic components form near the anode and the cathode, respectively, which causes long-term increases in the ionic strengths with respect to the initial values in these zones (Figure 3h). Supplementary Figure SM 1 shows the temporal evolution of the variables in Figure 3 for the solutions contained in the anode and cathode wells; the developments are consistent with the expectations.

Two observable phenomena in the ionic distributions are especially interesting. First, in nearly three quarters of the simulated domain, the ionic strength is less than the initial strength after three days of simulation, which shows the progressive desalination system that was shown in the results of other authors [49-51]. Second, the CO_3^{2-} component has an anomalous distribution with a significant concentration peak in the centre of the domain and not at the anode, as would be expected for an anion. In the equilibrium of carbonates in a closed system [52], the bicarbonate ion, HCO_3^- , only is predominant at pH values between 6.3 and 10.25. Behind the basic front, the main species is the carbonate ion (CO_3^{2-}), and behind the acidic front is predominant species is $H_2CO_3^*$ (treated as a non-volatile acid sum of the concentrations of the H_2CO_3 acid and the dissolved CO_2). The modelled behaviour of both HCO_3^- and CO_3^{2-} is consistent with the distributions of the rest of charged species (Figures 4a and 4b, respectively). However, the distribution of carbonic acid ($H_2CO_3^*$, Figure 4c) causes the total concentration of the carbonates to have the characteristic accumulation before the pH front (Figure 3b). The reason for this phenomenon can be determined from the various components of the total flow of carbonates. Only the $H_2CO_3^*$ species is present in the acidic zone, which does not move

by electromigration but rather by advective flow of the liquid phase (hydraulic flow and electro-osmotic flow) and by the diffusive/dispersive flux of the species. Moreover, the flow of the carbonates that have a net negative electrical charge (HCO_3^- and CO_3^{2-}) is dominated by electromigration. The final profile of the total flux of the CO_3^{2-} component (Figure 4d) is positive from the anode to the pH front (flow to the right). From the pH front to the cathode, the total flux is negative (to the left). Because the pH front determines which secondary species of the family of carbonates is predominant in the solution, it also marks the main type of transport. Thus, the main component of flow in the acidic region is advective-diffusive, and the flow in the basic region is by electromigration. Both flows come together in the front and generate an accumulation zone of the H_2CO_3^* species (Figure 4c) and, consequently, of the total CO_3^{2-} component (Figure 3b).

Figure 4. Spatial distribution in the EGM at selected times of (a) molal concentration of the CO_3^{2-} species; (b) molal concentration of the HCO_3^- species; (c) molal concentration of the H_2CO_3 species; (d) total mass flux of the CO_3^{2-} component.

The other state variables of the system, such as the electrical potential and the fluid pressure in soil pores (Figure 5), behave as is expected theoretically and from the experimental results in the literature [53, 54]. Figure 5a shows that the initial distribution of the electrical potential is nearly linear, but its slope decreases near the anode and cathode and increases in the intermediate zone. This is due to the spatial distribution of the electrical conductivity (Figure 5b), which is high near the electrolyte wells and lower in the centre of the domain due to the redistribution of solutes and the ionic strength (Figure 3h). The liquid pressure decreases rapidly to negative values near the anode, which causes soil desaturation as described in the literature [55, 56]. Over the long term, the entire domain experiences unsaturated conditions due to the reduced hydraulic

permeability of the soil (clay CL), which leads to partially saturated conditions when the output electro-osmotic flow is greater than the input hydraulic flow.

Figure 5. Spatial distribution in the EGM at selected times of (a) electric potential, E ; (b) apparent electrical conductivity, σ_a ; (c) liquid pressure, P_L ; (d) degree of saturation, S_r .

The desaturation process influences the temporal evolution of the outgoing or incoming anode flow to the cathode (Figure 6). Throughout the simulated time interval, the liquid inputs to the cathodic well (outputs from the soil) are greater than the outputs of the anodic well (inputs to the soil). Consequently, desaturation occurs near the anodic well and then spreads to the entire domain, as was discussed in the previous paragraph. When the partially saturated conditions reach the vicinity of the cathodic well, the incoming flow to the well by hydraulic flow decreases to zero and becomes outgoing due to the suction gradient. This compensates for the increased electro-osmotic flow towards the cathode

well (Figures 5c and 5d). The flows out of the anode and into the cathode equalise, and a steady state is reached. The difference between the values of the electro-osmotic flows, which are always higher near the cathode than near the anode, occurs because the electric conductivity is higher in the latter, the electric potential gradient is lower, and consequently the flow produced by the gradient is also lower.

Figure 6. Total liquid fluxes in the electrolyte wells (a) anodic well outflux (b) cathodic well influx.

3.3. EGM vs SGM simulations

The previous section showed that the M4EKR model for the EGM allows the main behaviour of EKR processes in soils to be characterised. However, other authors [13, 14, 48] have also reproduced some of these trends with simpler geochemical models (e.g., desaturation, differences in the decrease in the electrical potential and the electro-osmotic flow). Therefore, the question arises as to whether it is necessary to add complexity to numerical models to correctly simulate EKR in natural soils and porewaters. To

demonstrate the suitability of this simulation, an SGM simulation is performed to make critical comparisons with the EGM results.

A SGM composed solely of the components Na^+ , Cl^- , H_2O and H^+ is developed by adopting the parameters in Table 3 and the initial conditions in Table 4. We first compared the pH, which is essential to understanding the speciation in the EGM and to assessing the efficiencies of different physical and chemical processes that take place when these remediation techniques are applied [57]. Figure 7 compares the temporal evolution of the pH in the anodic and cathodic wells obtained with both geochemical models. In the SGM, the pH increases by approximately 3.5 at the anode and 2.3 at the cathode in 60 s. However, the variation in the EGM is much slower, and the pH only reaches the SGM values after 10 h of simulation. This phenomenon can be explained by the buffer system of carbonates, which is capable of maintaining the pH at relatively stable values even with small additions of acids or bases. For this reason, the temporal evolutions of both models are markedly different until 10 hours have passed, after which the buffering ceases to have an effect because of the nearly complete disappearance of bicarbonates in the domain.

Figure 7. *pH* evolution in the anodic and cathodic wells in the EGM and the SGM.

If different *pH* profiles are observed at various times (Figure 8), the forward speed of the fronts is much faster in the SGM; the front is already well-defined in 1 hour compared to the 3 hours required in the EGM. H^+ is a conservative solute in the SGM, whereas it is significantly delayed in the EGM due to the buffering effect of the carbonate system. This effect can be seen more clearly with the help of Figure 9. Points A and B represent the mean locations of the acidic and basic fronts within the domain, respectively. Their positions (x_A , x_B) were calculated using the expressions

$$pH(x_A, t) = pH_{ini} - \Delta pH_{acidic}(t)/2 \quad (46)$$

$$pH(x_B, t) = pH_{ini} + \Delta pH_{basic}(t)/2 \quad (47)$$

where pH_{ini} is the initial *pH* value, t the time, and the *pH* increments were calculated as

$$\Delta pH_{acidic}(t) = pH_{ini} - pH_{min}(t) \quad (48)$$

$$\Delta pH_{basic}(t) = pH_{max}(t) - pH_{ini} \quad (49)$$

where $pH_{\max}(t)$ and $pH_{\min}(t)$ are the maximum and minimum values of the pH profile at time t . Initially, the points A and B are located in the extremes of the domain, but when the pH front is fully formed, their positions are nearly coincident. If the evolution of the positions of the fronts is represented by the locations of these points, the disparity in the speeds of advancement of the fronts can also be observed (Figure 10). In the EGM, the advancement of the acidic front is nearly zero until 1 h has elapsed, whereas in the SGM, the pH front has already formed almost 10 cm from the anodic well at that time. In the EGM, the front takes more than one additional hour to form and does so at a more central position. In both cases, the front stops moving towards the cathode at similar speeds, although it reaches closer to the cathode positions in the SGM. This buffering capacity was experimentally observed in soils with a significant carbonate mineral content [58, 59]. During the electrokinetic treatment of a heavy metal contaminated soil, the dissolution of those minerals in the proximity of the anode produced the neutralization of the acid front. The pH values remained closed to neutrality and, consequently, the speciation of the heavy metals was significantly altered. In the present work, the different pH profiles also have an immediate effect on speciation and alter the distributions of secondary species of interest. Supplementary Figures SM 2 to SM 4 compare the normalised concentrations of several secondary species of Na^+ in the EGM and SGM.

Figure 8. pH profiles in the EGM and in the SGM at selected times.

Figure 9. Proposed mean location of the acidic (point A) and basic (point B) fronts.

4. CONCLUSIONS

This paper proposed a conceptual model for the behaviour of an electrokinetic soil remediation system. Mass balance, chemical equilibrium, and constitutive equations were proposed. The formulation was applied to simulate the behaviour of a one-dimensional system that reproduces the configuration of a simple reactor. Two geochemical systems were considered. The first, the EGM, takes into account a realistic composition of natural porewater. The SGM, which has the same pH and concentration of mobile charges, assumes an idealised porewater composition with only four components (Na^+ , Cl^- , H_2O and H^+). The behavioural trends obtained with these models are consistent with those described by previous studies, including a long-term desaturation of the domain, a larger decrease in the electrical potential near the cathode, and greater electro-osmotic flow towards the cathode well. However, there are significant discrepancies between the EGM and the SGM with respect to the pH, which can be considered the primary control variable in the soil remediation process. A different early temporal evolution of the pH is observed, which is much faster in the SGM. This causes much faster shifts in the basic and acidic fronts, and the final equilibrium is shifted towards the cathode well. This behaviour is caused by the buffering capacity of the system of carbonates in natural waters, which has not been considered in other models (such as the SGM). Buffering due to carbonates significantly affects the evolution, pH distribution, and ultimately the process efficiency of electrokinetic remediation because it affects the speciation of contaminants, the adsorption or desorption of soil particles, and their mobility or that of the liquid phase that contains them. Therefore, if numerical models are used to design actual remediation systems, previous simulations that use simplified geochemical systems may produce results that are significantly different from those obtained in reality. The delay in the formation and movement of pH fronts can cause greater energy consumption and duration

of the remediation process than those expected by simple geochemical modelling. Therefore, it is important to include a complete geochemical model in electrokinetic remediation models to properly understand all of the processes that occur in natural soils and porewaters and to thus evaluate the efficiency of remediation technologies.

SUPPLEMENTARY MATERIAL

We included a notation list and some additional figures on the evolution of the total concentrations of the components and other variables in the electrolyte wells obtained with the EGM and the spatial distributions of different species of the Na^+ component obtained with the EGM and the SGM in the Supplementary Material.

ACKNOWLEDGEMENTS

This work was supported by the European Union [project FEDER OP2014-2020 of Castilla-La Mancha]; and by the Spanish Government [project CTM2013-45612-R].

REFERENCES

- [1] Y.B. Acar, Principles of electrokinetic remediation, *Environ. Sci. Technol.*, 27 (1993) 2638-2647.
- [2] A.T. Yeung, S. Datla, Fundamental formulation of electrokinetic extraction of contaminants from soil, *Can. Geotech. J.*, 32 (1995) 569-583.
- [3] F.L. Souza, C. Saéz, J. Llanos, M.R.V. Lanza, P. Cañizares, M.A. Rodrigo, Solar-powered electrokinetic remediation for the treatment of soil polluted with the herbicide 2,4-D, *Electrochim. Acta*, 190 (2016) 371-377.

- [4] S. Yuan, Z. Zheng, J. Chen, X. Lu, Use of solar cell in electrokinetic remediation of cadmium-contaminated soil, *J. Hazard. Mater.*, 162 (2009) 1583-1587.
- [5] M. Zhou, S. Zhu, Y. Liu, X. Wang, Removal of fluorine from contaminated soil by electrokinetic treatment driven by solar energy, *Environ. Sci. Pollut. Res.*, 20 (2013) 5806-5812.
- [6] P.C. Renaud, R.F. Probstein, Electroosmotic control of hazardous wastes, *Physicochem. Hydrodyn.*, 6th Int Conf, Dedicated to the Memory of Veniamin Levich, 9 (1987) 345-360.
- [7] A.P. Shapiro, P.C. Renaud, R.F. Probstein, Preliminary studies on the removal of chemical species from saturated porous media by electroosmosis, *PCH, PhysicoChem. Hydrodyn.*, 11 (1989) 785-802.
- [8] A.P. Shaplo, R.F. Probstein, Removal of contaminants from saturated clay by electroosmosis, *Environ. Sci. Technol.*, 27 (1993) 283-291.
- [9] J.M. Paz-Garcia, K. Baek, I.D. Alshawabkeh, A.N. Alshawabkeh, A generalized model for transport of contaminants in soil by electric fields, *J. Environ. Sci. Health, Part A: Toxic/Hazard. Subst. Environ. Eng.*, 47 (2012) 308-318.
- [10] S.K. Puppala, A.N. Alshawabkeh, Y.B. Acar, R.J. Gale, M. Bricka, Enhanced electrokinetic remediation of high sorption capacity soil, *J. Hazard. Mater.*, 55 (1997) 203-220.
- [11] K.R. Reddy, U.S. Parupudi, S.N. Devulapalli, C.Y. Xu, Effects of soil composition on the removal of chromium by electrokinetics, *J. Hazard. Mater.*, 55 (1997) 135-158.
- [12] R.A. Jacobs, M.Z. Sengun, R.E. Hicks, R.E. Probstein, Model and Experiments on Soil Remediation by Electric Fields, *J. Environ. Sci. Health, Part A: Environ. Sci. Eng.*, 29 (1994) 1933-1955.

- [13] R.A. Jacobs, R.F. Probstein, Two-Dimensional Modeling of Electroremediation, *AIChE J.*, 42 (1996) 1685-1696.
- [14] A.N. Alshawabkeh, Y.B. Acar, Electrokinetic remediation. II: Theoretical model, *J. Geotech. Eng.*, 122 (1996) 186-196.
- [15] A.N. Alshawabkeh, Y.B. Acar, Removal of contaminants from soils by electrokinetics: A theoretical treatise, *J. Environ. Sci. Health, Part A: Environ. Sci. Eng.*, 27 (1992) 1835-1861.
- [16] Y.B. Acar, A.N. Alshawabkeh, R.J. Gale, Fundamental aspects of electrokinetic remediation of soils, *Waste Manage.*, 13 (1993).
- [17] M. Mascia, S. Palmas, A.M. Polcaro, A. Vacca, A. Muntoni, Experimental study and mathematical model on remediation of Cd spiked kaolinite by electrokinetics, *Electrochim. Acta*, 52 (2007) 3360-3365.
- [18] C. Vereda-Alonso, J.M. Rodríguez-Maroto, R.A. García-Delgado, C. Gómez-Lahoz, F. García-Herruzo, Two-dimensional model for soil electrokinetic remediation of heavy metals: Application to a copper spiked kaolin, *Chemosphere*, 54 (2004) 895-903.
- [19] C. Vereda-Alonso, C. Heras-Lois, C. Gomez-Lahoz, F. Garcia-Herruzo, J.M. Rodriguez-Maroto, Ammonia enhanced two-dimensional electrokinetic remediation of copper spiked kaolin, *Electrochim. Acta*, 52 (2007) 3366-3371.
- [20] A.B. Ribeiro, J.M. Rodriguez-Maroto, E.P. Mateus, H. Gomes, Removal of organic contaminants from soils by an electrokinetic process: the case of atrazine. Experimental and modeling, *Chemosphere*, 59 (2005) 1229-1239.
- [21] E.D. Mattson, R.S. Bowman, E.R. Lindgren, Electrokinetic ion transport through unsaturated soil: 1. Theory, model development, and testing, *J. Contam. Hydrol.*, 54 (2002) 99-120.

- [22] E.D. Mattson, R.S. Bowman, E.R. Lindgren, Electrokinetic ion transport through unsaturated soil: 2. Application to a heterogeneous field site, *J. Contam. Hydrol.*, 54 (2002) 121-140.
- [23] A.Z. Al-Hamdan, K.R. Reddy, Electrokinetic remediation modeling incorporating geochemical effects, *J. Geotech. Geoenviron. Eng.*, 134 (2008) 91-105.
- [24] M.T. van Genuchten, Closed-form equation for predicting the hydraulic conductivity of unsaturated soils, *Soil Sci. Soc. Am. J.*, 44 (1980) 892-898.
- [25] J.K. Mitchell, K. Soga, *Fundamentals of soil behavior*, John Wiley & Sons, Inc, Hoboken, New Jersey, USA, 2005.
- [26] R.H. Brooks, A.T. Corey, *Hydraulic Properties of Porous Media*, Colorado State University 1964.
- [27] C.M. Bethke, *Geochemical and Biogeochemical Reaction Modeling*, Cambridge University Press, New York, USA, 2008.
- [28] H. Chou, L. Wu, L. Zeng, A. Chang, Evaluation of solute diffusion tortuosity factor models for variously saturated soils, *Water Resour. Res.*, 48 (2012) W10539.
- [29] J. Bear, *Dynamics of Fluids in Porous Media*, Dover, 1972.
- [30] J.O.M. Bockris, A.K.N. Reddy, *Modern Electrochemistry. Volume 1. An Introduction to an Interdisciplinary Area*, Springer, New York, N.Y, USA, 1970.
- [31] J.D. Rhoades, N.A. Manteghi, P.J. Shouse, W.J. Alves, Soil Electrical Conductivity and Soil Salinity: New Formulations and Calibrations, *Soil Sci. Soc. Am. J.*, 53 (1989) 433-439.
- [32] S.P. Friedman, Soil properties influencing apparent electrical conductivity: A review, *Comput. Electron. Agric.*, 46 (2005) 45-70.
- [33] C.A.J. Appelo, Specific conductance: how to calculate, to use, and the pitfalls. , (2010).

- [34] D.L. Parkhurst, User's guide to PHREEQC - A computer program for speciation, reaction-path, advective-transport, and inverse geochemical calculations, User's Guide to PHREEQC (Version 2) - A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations, (1995).
- [35] R.M. Garrels, C.L. Christ, Solutions, minerals, and equilibria, Harper & Row, 1965.
- [36] COMSOL AB, COMSOL Multiphysics Reference Manual Version: COMSOL 5.1, 2015.
- [37] Ö. Babur, V. Smilauer, T. Verhoeff, M. Van Den Brand, A survey of open source multiphysics frameworks in engineering in: J. Dongarra, S. Koziel, L. Leifsson, M. Lees, V.V. Krzhizhanovskaya, P.M.A. Sloot (Eds.) International Conference on Computational Science, ICCS 2015, Elsevier, Reykjavík, Iceland, 2015, pp. 1088-1097.
- [38] D.L. Brown, J. Bell, D. Estep, W. Gropp, B. Hendrickson, S. Keller-McNulty, D. Keyes, J.T. Oden, L. Petzold, M. Wright, Applied Mathematics at the U.S. Department of Energy: Past, Present and a View to the Future, Lawrence Livermore National Laboratory (LLNL), Livermore, CA, USA, 2008, pp. 29.
- [39] D.E. Keyes, L.C. McInnes, C. Woodward, W. Gropp, E. Myra, M. Pernice, J. Bell, J. Brown, A. Clo, J. Connors, E. Constantinescu, D. Estep, K. Evans, C. Farhat, A. Hakim, G. Hammond, G. Hansen, J. Hill, T. Isaac, X. Jiao, K. Jordan, D. Kaushik, E. Kaxiras, A. Koniges, K. Lee, A. Lott, Q. Lu, J. Magerlein, R. Maxwell, M. McCourt, M. Mehl, R. Pawlowski, A.P. Randles, D. Reynolds, B. Rivière, U. Rüde, T. Scheibe, J. Shadid, B. Sheehan, M. Shephard, A. Siegel, B. Smith, X. Tang, C. Wilson, B. Wohlmuth, Multiphysics simulations: Challenges and opportunities, Int. J. High Perform. Comput. Appl., 27 (2013) 4-83.
- [40] F. Palacios, J. Alonso, K. Duraisamy, M. Colonno, J. Hicken, A. Aranake, A. Campos, S. Copeland, T. Economon, A. Lonkar, T. Lukaczyk, T. Taylor, Stanford

University Unstructured (SU2): An open-source integrated computational environment for multi-physics simulation and design, 51st AIAA Aerospace Sciences Meeting including the New Horizons Forum and Aerospace Exposition, American Institute of Aeronautics and Astronautics 2013.

[41] M.K. Gobbert, A. Churchill, G. Wang, T.I. Seidman, COMSOL Multiphysics for efficient solution of a transient reaction-diffusion system with fast reaction, in: Y. Rao (Ed.) COMSOL Conference 2009 Boston, USA, 2009.

[42] V. Navarro, L. Asensio, T. Yustres, X. Pintado, J. Alonso, An elastoplastic model of bentonite free swelling, Eng. Geol. (Amsterdam, Neth.), 181 (2014) 190-201.

[43] V. Navarro, L. Asensio, A. Yustres, G. De la Morena, X. Pintado, Swelling and mechanical erosion of MX-80 bentonite: Pinhole test simulation, Eng. Geol. (Amsterdam, Neth.), 202 (2016) 99-113.

[44] R. López-Vizcaíno, V. Navarro, M.J. León, C. Risco, M.A. Rodrigo, C. Sáez, P. Cañizares, Scale-up on electrokinetic remediation: Engineering and technological parameters, J. Hazard. Mater., 315 (2016) 135-143.

[45] E.C. Leong, S. Tripathy, H. Rahardjo, Total suction measurement of unsaturated soils with a device using the chilled-mirror dew-point technique, Geotechnique, 53 (2003) 173-182.

[46] E. Giffaut, M. Grivé, P. Blanc, P. Vieillard, E. Colàs, H. Gailhanou, S. Gaboreau, N. Marty, B. Madé, L. Duro, Andra thermodynamic database for performance assessment: ThermoChimie, Appl. Geochem., 49 (2014) 225-236.

[47] M.J. Pikal, Ion-pair formation and the theory of mutual diffusion in a binary electrolyte, J. Phys. Chem., 75 (1971) 663-675.

- [48] C.A. Confederación Hidrográfica del Guadiana, Programa de seguimiento de las aguas subterráneas. Control de Vigilancia, Ministerio de Agricultura, Alimentación y Medio Ambiente, 2015.
- [49] G. Skibsted, L.M. Ottosen, P.E. Jensen, J.M. Paz-Garcia, Electrochemical desalination of bricks – Experimental and modeling, *Electrochim. Acta*, 181 (2015) 24-30.
- [50] J.M. Paz-García, B. Johannesson, L.M. Ottosen, A.N. Alshawabkeh, A.B. Ribeiro, J.M. Rodríguez-Maroto, Modeling of electrokinetic desalination of bricks, *Electrochim. Acta*, 86 (2012) 213-222.
- [51] J.M. Paz-García, B. Johannesson, L.M. Ottosen, A.B. Ribeiro, J.M. Rodríguez-Maroto, Simulation-based analysis of the differences in the removal rate of chlorides, nitrates and sulfates by electrokinetic desalination treatments, *Electrochim. Acta*, 89 (2013) 436-444.
- [52] W. Stumm, J.J. Morgan, *Aquatic Chemistry*, 3rd ed., John Wiley & Sons, New York, 1996.
- [53] L. Gabrieli, A.N. Alshawabkeh, Influence of boundary conditions on transient excess pore pressure during electrokinetic applications in soils, *J. Appl. Electrochem.*, 40 (2010) 1113-1121.
- [54] A.N. Alshawabkeh, T.C. Sheahan, X. Wu, Coupling of electrochemical and mechanical processes in soils under DC fields, *Mech. Mater.*, 36 (2004) 453-465.
- [55] S. Wiczorek, H. Weigand, M. Schmid, C. Marb, Electrokinetic remediation of an electroplating site: design and scale-up for an in-situ application in the unsaturated zone, *Eng. Geol. (Amsterdam, Neth.)*, 77 (2005) 203-215.
- [56] J. Yuan, M.A. Hicks, Influence of gas generation in electro-osmosis consolidation, *Int. J. Numer. Anal. Methods Geomech.*, (2016).

- [57] R.E. Saichek, K.R. Reddy, Effect of pH control at the anode for the electrokinetic removal of phenanthrene from kaolin soil, *Chemosphere*, 51 (2003) 273-287.
- [58] A.Z. Al-Hamdan, K.R. Reddy, Transient behavior of heavy metals in soils during electrokinetic remediation, *Chemosphere*, 71 (2008) 860-871.
- [59] A.Z. Al-Hamdan, K.R. Reddy, Geochemical assessment of metal transport in glacial till during electrokinetic remediation, *Environ. Monit. Assess.* 139 (2008) 137-149.

Supplementary materials

Notation list

Parameters	Description	Units
a_i	activity of species i	mol kg_w^{-1}
C_m	total molal concentration of component m	mol kg_w^{-1}
C_m^o	initial molal concentration of component m	mol kg_w^{-1}
C_m^A	total molal concentration of component m in the anodic well	mol kg_w^{-1}
C_m^C	total molal concentration of component m in the cathodic well	mol kg_w^{-1}
c_i	molal concentration of species i	mol kg_w^{-1}
D_i^e	effective diffusion coefficient of species i	m^2s^{-1}
D_i^o	diffusion coefficient in water of species i	m^2s^{-1}
D_i	diffusion/dispersion coefficient of species i	m^2s^{-1}
E	electric potential	V
F	Faraday constant	C mol^{-1}
g	gravity constant	m s^{-1}
I	ionic strength	mol kg_w^{-1}
i	total current density	A m^{-2}
i	species index	--
K_{sat}^h	saturated hydraulic permeability	m s^{-1}
K_e^h	effective hydraulic permeability	m s^{-1}
K_e^{eo}	effective electroosmotic permeability	$\text{m}^2 \text{V}^{-1} \text{s}^{-1}$
$\mathbf{l}_w$	total mass flux of water	$\text{kg m}^{-2} \text{s}^{-1}$
$\mathbf{l}_w^h$	mass flux of water, Darcian contribution	$\text{kg m}^{-2} \text{s}^{-1}$
$\mathbf{l}_w^{\text{eo}}$	mass flux of water, electroosmotic contribution	$\text{kg m}^{-2} \text{s}^{-1}$
$\mathbf{l}_m$	total molar flux of component m	$\text{mol m}^{-2} \text{s}^{-1}$
$\mathbf{l}_m^h$	molar flux of component m , Darcian contribution	$\text{mol m}^{-2} \text{s}^{-1}$
$\mathbf{l}_m^{\text{eo}}$	molar flux of component m , electroosmotic contribution	$\text{mol m}^{-2} \text{s}^{-1}$
$\mathbf{l}_m^{\text{em}}$	molar flux of component m , electromigration contribution	$\text{mol m}^{-2} \text{s}^{-1}$

$\mathbf{l}_m^{\text{dif}}$	molar flux of component m , Fickian contribution	$\text{mol m}^{-2} \text{s}^{-1}$
M	total number of components	--
M_m^A	moles of component m in anodic well	mol
$\dot{M}_m^{\text{in}A}$	inlet molar flow of component m in anodic well	mol s^{-1}
$\dot{M}_m^{\text{out}A}$	outlet molar flow of component m in anodic well	mol s^{-1}
M_m^C	moles of component m in cathodic well	mol
$\dot{M}_m^{\text{in}C}$	inlet molar flow of component m in cathodic well	mol s^{-1}
$\dot{M}_m^{\text{out}C}$	outlet molar flow of component m in cathodic well	mol s^{-1}
m	component index	--
m_w	water mass per unit of total volume of soil	kg m^{-3}
m_m	mass of component m por unidad de volumen	mol m^{-3}
m_{VG}	parameter of the Van Genuchten retention curve	--
N	total number of species	--
$\mathbf{n}$	normal vector	
n_{VG}	parameter of the Van Genuchten retention curve	--
P_G	gas pressure	kPa
P_L	liquid pressure	kPa
$\mathbf{q}_w$	total volumetric flux of water	$\text{m}^3 \text{m}^{-2} \text{s}^{-1}$
$\mathbf{q}_w^h$	Darcian volumetric flux of water	$\text{m}^3 \text{m}^{-2} \text{s}^{-1}$
$\mathbf{q}_w^{\text{eo}}$	electroosmotic volumetric flux of water	$\text{m}^3 \text{m}^{-2} \text{s}^{-1}$
$\mathbf{q}_i^{\text{em}}$	migration velocity of species i	m s^{-1}
Q	total electric charge	C m^{-3}
R	ideal gas constant	??
R_m	rate of production/consumption of component m	$\text{mol m}^{-3} \text{s}^{-1}$
R_Q	rate of generation/consumption of electric charge	$\text{C m}^{-3} \text{s}^{-1}$
R_m^A	rate of production/consumption of component m in anodic well	mol s^{-1}
R_m^C	rate of production/consumption of component m in cathodic well	mol s^{-1}
Sr	saturation degree	--
S^A	anodic surface	m^2

S^C	cathodic surface	m^2
s	matric suction	kPa
T	temperature	K
V^A	anolyte volume	m^3
V^C	catholyte volume	m^3
z	vertical coordinate	m
z_i	charge number of species i	
α_{VG}	parameter of the Van Genuchten retention curve	kPa^{-1}
α_i^m	molar contribution of component m to the production of species i	--
γ_i	activity coefficient of species i	--
δ_i^L	longitudinal dispersivity of species i	m
$\lambda_{\text{o},i}$	ionic molal conductivity of species i	$\text{S kg}_w \text{m}^{-1} \text{mol}^{-1}$
μ_i^e	effective ionic mobility of species i	$\text{m}^2 \text{V}^{-1} \text{s}^{-1}$
μ_i^o	ionic mobility of species i at infinite dilution in water	$\text{m}^2 \text{V}^{-1} \text{s}^{-1}$
ρ_w	water density	kg m^{-3}
σ_a	aparent electrical conductivity	S m^{-1}
σ_s	electrical conductivity of solid phase	S m^{-1}
σ_a	electrical conductivity of aqueous phase	S m^{-1}
τ	tortuosity	--
ϕ	porosity	--
φ_m^A	mol of m produced per mol of changed electrons in anodic surface	-
φ_m^C	mol of m produced per mol of changed electrons in cathodic surface	-
$\partial/\partial t$	time-derivative operator	s^{-1}
$\nabla \cdot$	divergence operator	m^{-1}
∇	gradient operator	m^{-1}

Figure SM 1. Evolution in the electrolyte wells for the EGM of (a) pH ; (b) total normalised concentration of the CO_3^{2-} component; (c) total normalised concentration of the SO_4^{2-} component; (d) total normalised concentration of the Na^+ component; (e) total normalised concentration of the K^+ component; (f) total normalised concentration of the Ca^{2+} component; (g) total normalised concentration of the Mg^{2+} component; (h) Ionic strength, I .

Figure SM 2. Spatial distribution of the normalised concentration of the species Na^+ in the EGM and the SGM at selected times.

Figure SM 3. Spatial distribution of the normalised concentration of the species NaOH in the EGM and the SGM at selected times.

Figure SM 4. Spatial distribution of the normalised concentration of the species NaCl in the EGM and the SGM at selected times.