Calcite buffer effects in electrokinetic remediation of clopyralid-polluted soils

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ABSTRACT

This work presents a study of the dissolution-precipitation processes of calcite in soil undergoing electrokinetic remediation processes. For this purpose, a numerical inspection of one of these processes in a calcareous soil (10% calcite content) contaminated with an of the organochlorine acid herbicide (3,6-dichloro-2-pyridinecarboxylic acid) was carried out. The numerical tool used to perform this analysis was the Multiphysics for EKR (M4EKR), a module programmed by the authors in the COMSOL Multiphysics platform.

A detailed analysis of the pH, the distribution of species that have a significant influence on soil buffering capacity (carbonates and calcite), as well as the pollutant, has been performed. In this way, the kinetics of the calcite dissolution-precipitation processes have been analysed in order to determine the pH of the water in the pores and, therefore, how it directly affects the effectiveness of the treatment. Additionally, a sensitivity analysis of the selected EKR process has been carried out at different values of the rate of calcite dissolution due to the uncertainty associated with the reactive surface area parameter.

KEYWORDS

Electrokinetic soil remediation, Multiphysics simulation, soil buffering capacity, herbicide, M4EKR, calcite
1. INTRODUCTION

The application of an electrical potential gradient between electrodes located in a soil activates a series of electrokinetic transport mechanisms capable of mobilising water (electroosmosis), ionic species (electromigration) and even charged particles (electrophoresis). Specifically, this technique is called electrokinetic remediation (EKR) when it is applied to contaminated soils with the aim of mobilizing polluting species to controlled extraction points [1-4]. The coupling of the above-mentioned transport mechanisms and the fact that, these treatments can be successfully applied in soils with low hydraulic permeability, where Darcy flow is very limited, makes EKR technology a very versatile technique and consequently, an efficient and competitive alternative for treating pollution events with different compounds such as heavy metals [5-8], PAH [9-13] or pesticides [14-18].

Regarding the EKR processes, the electrolysis of water is also an important electrochemical reaction developed on the electrode surface. This process simultaneously generates high concentrations of protons (H\(^+\)) by the oxidation reaction of water on the anodic surface and hydroxyl ions (OH\(^-\)) in the cathodic reduction reaction. The changes in the concentration of H\(^+\) and OH\(^-\) are reflected in the generation of an important pH gradient in the soil located between anodes and cathodes.

The pH changes generated in the vicinity of the electrodes depend on the amount of electro-generated H\(^+\) and OH\(^-\) and, in turn, on the electrical potential gradient applied in the process. However, the pH-variations observed in the rest of the domain are determined by the mobility of the acidic and alkaline fronts, from the anodic and cathodic zones respectively. The transport of the pH front is mainly due to the electromigratory flow of H\(^+\) and OH\(^-\) species to the opposite sign electrodes and advective/diffusive processes, all of which are strongly influenced by soil buffering capacity [19-24]. Generally, soil
buffering capacity is defined by the contribution of different processes: (i) protonation/deprotonation of substances present in the porewater, (ii) adsorption/desorption and ion exchange between the soil and the porewater and (iii) dissolution-precipitation of minerals [25].

At this point it is important to stress the importance of pH changes in EKR treatments. This variable directly influences the chemical speciation of the substances present in soil and porewater, conditioning their ionic nature. Consequently, the pH of the system can determine the predominant mechanism of transport of chemical species in the soil.

In order to have a global understanding of the evolution of pH in an EKR process, it is necessary to improve the knowledge of the interactions attained between the electrokinetic transport phenomena and the physical, chemical and electrochemical processes that take place in an EKR treatment. The main objective of this work is to evaluate the influence of soil buffering capacity on the performance of an EKR process.

For this purpose, a numerical analysis of the EKR treatment of a calcareous soil with a calcite content of 10%, contaminated with clopyralid (3,6-dichloro-2-pyridinecarboxylic acid, a common acid herbicide) was performed. Specifically, this study has evaluated the effects generated by the calcite dissolution-precipitation processes on the general behaviour of the EKR process and their importance for a better understanding of this type of treatment.

The numerical tool used was the M4EKR module, Multiphysics for EKR [26]. M4EKR is a numerical model developed by the authors as a result of the knowledge gained over the last years in the treatment of contaminated soils using electrokinetic techniques [27-35]. The M4EKR model has been implemented in COMSOL Multiphysics and is capable of simulating the general behaviour trends of an EKR process by solving a coupled
problem of reactive transport and electric field. This makes the M4EKR module a powerful computational tool that has been used to carry out different studies [36-38].

In this work, an assessment of the spatial distribution of the concentration of the species that have a significant influence on soil buffering capacity (carbonates and calcite) was performed. The relationship between the observed behaviour and the pH profiles obtained is also analysed, as well as the direct influence on the performance of the simulated EKR process. Additionally, and due to the difficulties in accurately predicting the kinetics of calcite dissolution-precipitation, associated with the uncertainty of the reactive surface area [39], a sensitivity analysis of the selected EKR process was performed using different values of this parameter, which is equivalent to different levels of the rate of calcite dissolution. Consequently, this study provides useful information on the influence of soil buffer capacity on the general performance of an EKR process applied to the decontamination of a calcareous soil with acidic contaminants.

2. CONCEPTUAL MODEL AND NUMERICAL IMPLEMENTATION

M4EKR is a reactive transport model applied to unsaturated porous media. It is a very flexible numerical tool. Its adaptability and capacity for gradual implementation of improvements are easy by the fact that the base module has been programmed in a multiphysical environment. [26].

For conceptual simplification, the M4EKR version employed in this work does not consider gas transport and the deformability of the soil. Due to the small scale of the simulated tests (laboratory scale), it is acceptable to assume isothermal conditions (298 K). Given these simplifications, it is clear that the model will not perfectly match the actual behaviour in an EKR process. However, this is not a limitation in the scope of the work, since the aim is to improve phenomenological understanding and not to replicate a
real case. Soil buffering capacity is provided by: chemical reactions with proton consumption/production (see Table 4), and dissolution-precipitation of calcite [40]. The adsorption/desorption processes onto the soil were not consider. As a novelty, the M4EKR version used in this work has been improved with the implementation of a kinetic model of calcite dissolution/precipitation, extrapolable to any other mineral if present.

Appendix A presents the basic mathematical formulation employed in module M4EKR. A more detailed description of the formulation can be found in literature [26].

2.1. Calcite mass balance

The evolution of the mass of calcite is obtained solving the mass balance equation

\[
\frac{dM_{\text{calcite}}}{dt} = R_{\text{calcite}}
\]

where \( M_{\text{calcite}} \) is the total mass of calcite (mol/m\(^3\)) and \( R_{\text{calcite}} \) is the calcite production/consumption rate (mol m\(^3\) s\(^{-1}\)).

2.2. Kinetic of calcite precipitation/dissolution

The calcite production/consumption rate, \( R_{\text{calcite}} \) (mol m\(^3\) s\(^{-1}\)), has been estimated by a general equation provided by Lasaga [41]:

\[
R_{\text{calcite}} = \pm k_{\text{calcite}} \cdot \phi \cdot S r \cdot \rho_w \cdot S_{\text{calcite}} \cdot (1 - \Omega_{\text{calcite}}^{\theta})^\eta
\]

where \( k_{\text{calcite}} \) is the kinetic constant (mol s\(^{-1}\)m\(^2\)) of dissolution (negative value) or precipitation (positive value) processes, \( S_{\text{calcite}} \) is the reactive surface area (m\(^2\) kg\(^{-1}\)H\(_2\)O), and \( \Omega_{\text{calcite}} \) is the saturation ratio. Finally, \( \theta \) and \( \eta \) are empirical parameters that determine the relation between reaction rate and saturation ratio. The parameters selected for calcite were \( \theta = 0.5 \) and \( \eta = 2 \) [42]. A reference value for \( S_{\text{calcite}} \) was extracted from literature [42]. The parameters \( \phi, S r \) and \( \rho_w \) correspond to the soil porosity, saturation degree and
water density. The saturation ratio ($\Omega_{\text{calcite}}$) is estimated using the Eq. (3) where $K_{s, \text{calcite}}$

is the solubility constant of calcite [43] and IAP is the ionic activity product, calculated

as indicated in Eq. (4) where $a_{\text{Ca}^{2+}}$ and $a_{\text{CO}_3^{2-}}$ are the activities of $\text{Ca}^{2+}$ and $\text{CO}_3^{2-}$

respectively.

$$\Omega_{\text{calcite}} = \frac{\text{IAP}_{\text{calcite}}}{K_{s, \text{calcite}}} \quad \text{Eq. (3)}$$

$$\text{IAP}_{\text{calcite}} = a_{\text{Ca}^{2+}} \cdot a_{\text{CO}_3^{2-}} \quad \text{Eq. (4)}$$

The kinetic constant ($k_{\text{calcite}}$) has been defined using a model that takes into account the

influence additional mechanisms in the value of $k_{\text{calcite}}$. In this case, a dependence on the

activity $\text{HCO}_3^-$ has been observed for carbonate minerals such as calcite [42]. The

expression for $k_{\text{calcite}}$ reads as follows

$$k_{\text{calcite}} = k_{25}^{\text{calcite}} \cdot \exp\left[\frac{-E_{a, \text{calcite}}}{R} \left(\frac{1}{T} - \frac{1}{298.15}\right)\right] + k_{25}^{\text{HCO}_3^-} \cdot \exp\left[\frac{-E_{a, \text{HCO}_3^-}}{R} \left(\frac{1}{T} - \frac{1}{298.15}\right)\right] \cdot (a_{\text{HCO}_3^-})^{n_{\text{HCO}_3^-}}$$

$$\text{Eq. (5)}$$

where $E_{a, i}$ and $a_i$ are the activation energy (kJ mol$^{-1}$) and the activity, and $k_{25}^i$ and $n_i$ are model parameters for the species considered, in this particular case the mineral considered

(calcite) and $\text{HCO}_3^-$. Table 1 shows the numerical values of parameters for the kinetic

model selected [42].
### Table 1. Kinetic model parameters from calcite

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Units</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{25}^{\text{calcite}}$</td>
<td>mol m$^{-2}$ s$^{-1}$</td>
<td>$1.8 \times 10^{-7}$</td>
</tr>
<tr>
<td>$k_{25}^{\text{HCO}_3^-}$</td>
<td>mol m$^{-2}$ s$^{-1}$</td>
<td>$1.9 \times 10^{-3}$</td>
</tr>
<tr>
<td>$E_a^{\text{calcite}}$</td>
<td>kJ mol$^{-1}$</td>
<td>66</td>
</tr>
<tr>
<td>$E_a^{\text{HCO}_3^-}$</td>
<td>kJ mol$^{-1}$</td>
<td>67</td>
</tr>
<tr>
<td>$n_{\text{HCO}_3^-}$</td>
<td>-</td>
<td>1.63</td>
</tr>
<tr>
<td>$\theta$</td>
<td>-</td>
<td>0.5</td>
</tr>
<tr>
<td>$\eta$</td>
<td>-</td>
<td>2</td>
</tr>
<tr>
<td>$S_{\text{calcite}}$</td>
<td>m$^2$ kg$^{-1}$ H$_2$O</td>
<td>1.54</td>
</tr>
</tbody>
</table>

#### 3. NUMERICAL IMPLEMENTATION

The M4EKR model was implemented in COMSOL Multiphysics [44], a partial differential equation solver developed in a multiphysics environment. COMSOL uses the finite element method with Lagrange multipliers. One of its most remarkable attributes is its versatility, since the user has great freedom to define the system of equations required to solve the selected case [45-47].

M4EKR solves transport problems coupled with chemical speciation using a monolithic approach, without using any other external software. This strategy optimises the resources and reduces the computational cost. This aspect is of high importance and provides a novelty to this work because it is common to use operator-splitting procedures for solving reactive transport problems [48-50]. Furthermore, the computational capacity of the M4EKR module goes beyond this kind of codes since it also allows to solve simultaneously the partial differential equations that define the transport and balance of mass of water, mass of dissolved species and electric charge, (See Appendix A, Eqs. A.1, A.9 and A.10 respectively), the ordinary differential equations used to solve the mass
balance in electrolyte wells, (Eq. A.11) and the algebraic equations from the stoichiometric approach used in the chemical speciation.

4. SIMULATION OF THE EKR PROCESS

4.1. Modelled configuration

4.1.1. Polluted Soil

The electrokinetic remediation of a polluted soil with an organochlorine herbicide (20 mg of clopyralid kg\(^{-1}\) soil\(^{dry}\)) was analysed. The selected soil is a calcareous soil, (calcite mass fraction 10%). Table 2 presents the textural and mineralogical properties of the modelled soil. The soil parameters are show in Table 3. Bulk density and gravimetric water content are representative of the natural state of this soil [30].

Table 2. Textural and mineralogical properties of the modelled soil.

<table>
<thead>
<tr>
<th>Mineral Analysis</th>
<th>Mineral</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>Feldspar</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>Calcite</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Kaolinite</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>Smeecte</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>Illite</td>
<td>21</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Textural Parameters</th>
<th>Size fraction</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand</td>
<td>26.1</td>
<td></td>
</tr>
<tr>
<td>Silt</td>
<td>68.6</td>
<td></td>
</tr>
<tr>
<td>Clay</td>
<td>5.3</td>
<td></td>
</tr>
</tbody>
</table>

[30]
Table 3. Modelled soil parameters.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Description</th>
<th>Values</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_{VG}$</td>
<td>Parameter of the Van Genuchten[51] retention curve</td>
<td>0.0147</td>
<td>kPa$^{-1}$</td>
</tr>
<tr>
<td>$n_{VG}$</td>
<td>Parameter of the Van Genuchten[51] retention curve</td>
<td>1.2593</td>
<td>-</td>
</tr>
<tr>
<td>$m_{VG}$</td>
<td>Parameter of the Van Genuchten[51] retention curve</td>
<td>0.2059</td>
<td>-</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Porosity</td>
<td>0.4681</td>
<td>-</td>
</tr>
<tr>
<td>$K_{h}^{sat}$</td>
<td>Saturated hydraulic permeability</td>
<td>$2.03 \times 10^{-10}$</td>
<td>m s$^{-1}$</td>
</tr>
<tr>
<td>$K_{eo}^{sat}$</td>
<td>Saturated electroosmotic permeability</td>
<td>$2.4 \times 10^{-9}$</td>
<td>m$^2$ V$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$\rho_s$</td>
<td>Soil particle density</td>
<td>2681.5</td>
<td>kg m$^{-3}$</td>
</tr>
<tr>
<td>$\rho_{bulk}$</td>
<td>Bulk density</td>
<td>1894.4</td>
<td>kg m$^{-3}$</td>
</tr>
<tr>
<td>$w$</td>
<td>Moisture</td>
<td>0.32</td>
<td>kg water kg dry soil$^{-1}$</td>
</tr>
<tr>
<td>$\delta_i^{L}$</td>
<td>Longitudinal dispersivity of species $i$</td>
<td>0.01</td>
<td>m</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Vapour tortuosity</td>
<td>1.00</td>
<td>-</td>
</tr>
</tbody>
</table>

4.1.2. Porewater

The geochemical model implemented consists of 7 components and 20 secondary species. The chemical reactions and thermodynamic properties (equilibrium constants [43], hard-core diameters and diffusion coefficients) are presented in Table 4. The activity coefficients of the species were estimated by WATEQ Debye-Hückel model [52].
Table 4. Thermodynamic properties of the modelled geochemical systems

<table>
<thead>
<tr>
<th>Species</th>
<th>Reactions</th>
<th>log $K_{eq}$ (25ºC)</th>
<th>Hard core diameter / Å</th>
<th>$D_e$ / m²s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl⁻</td>
<td>Cl⁻</td>
<td>0</td>
<td>3.6</td>
<td>2.03×10⁻⁹</td>
</tr>
<tr>
<td>H₂O</td>
<td>H₂O</td>
<td>0</td>
<td>3.4</td>
<td>5.27×10⁻⁹</td>
</tr>
<tr>
<td>H⁺</td>
<td>H⁺</td>
<td>0</td>
<td>4.1</td>
<td>9.31×10⁻⁹</td>
</tr>
<tr>
<td>CO₃²⁻</td>
<td>CO₃²⁻</td>
<td>0</td>
<td>4.7</td>
<td>9.55×10⁻¹⁰</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>Ca²⁺</td>
<td>0</td>
<td>5.7</td>
<td>7.93×10⁻¹⁰</td>
</tr>
<tr>
<td>Na⁺</td>
<td>Na⁺</td>
<td>0</td>
<td>4.1</td>
<td>1.33×10⁻⁹</td>
</tr>
<tr>
<td>Clopy⁻</td>
<td>Clopy⁻</td>
<td>0</td>
<td>3.6</td>
<td>8.20×10⁻¹⁰</td>
</tr>
<tr>
<td>OH⁻</td>
<td>H₂O ↔ OH⁻ + H⁺</td>
<td>-14</td>
<td>3.6</td>
<td>5.27×10⁻⁹</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>CO₃²⁻ + H⁺ ↔ HCO₃⁻</td>
<td>10.33</td>
<td>3.6</td>
<td>1.18×10⁻⁹</td>
</tr>
<tr>
<td>H₂CO₃</td>
<td>CO₃²⁻ + 2H⁺ ↔ H₂CO₃</td>
<td>16.68</td>
<td>3.4</td>
<td>1.92×10⁻⁹</td>
</tr>
<tr>
<td>CaHCO₃⁺</td>
<td>Ca²⁺ + CO₃²⁻ + H⁺ ↔ CaHCO₃⁺</td>
<td>11.43</td>
<td>4.1</td>
<td>5.06×10⁻¹⁰</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>Ca²⁺ + CO₃²⁻ ↔ CaCO₃</td>
<td>3.22</td>
<td>3.4</td>
<td>4.46×10⁻¹⁰</td>
</tr>
<tr>
<td>Ca(OH)⁺</td>
<td>Ca²⁺ + H₂O ↔ Ca(OH)⁺ + H⁺</td>
<td>-12.78</td>
<td>4.1</td>
<td>2.13×10⁻¹⁰</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>Na⁺ + HCO₃⁻ ↔ NaHCO₃</td>
<td>10.08</td>
<td>3.4</td>
<td>6.73×10⁻¹⁰</td>
</tr>
<tr>
<td>NaCO₃</td>
<td>Na⁺ + CO₃²⁻ ↔ NaCO₃</td>
<td>1.27</td>
<td>3.6</td>
<td>5.85×10⁻¹⁰</td>
</tr>
<tr>
<td>NaOH</td>
<td>Na⁺ + H₂O ↔ NaOH + H⁺</td>
<td>-14.75</td>
<td>3.4</td>
<td>1.89×10⁻¹⁰</td>
</tr>
<tr>
<td>CaCl⁺</td>
<td>Ca²⁺ + Cl⁻ ↔ CaCl⁺</td>
<td>-0.29</td>
<td>4.1</td>
<td>2.13×10⁻¹⁰</td>
</tr>
<tr>
<td>NaCl</td>
<td>Na⁺ + Cl⁻ ↔ NaCl</td>
<td>-0.5</td>
<td>3.4</td>
<td>1.89×10⁻¹⁰</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>Ca²⁺ + 2 Cl⁻ ↔ CaCl₂</td>
<td>-0.64</td>
<td>3.4</td>
<td>7.54×10⁻¹⁰</td>
</tr>
<tr>
<td>Clopy⁺</td>
<td>Clopy⁺ + H⁺ ↔ Clopy</td>
<td>2.32</td>
<td>3.4</td>
<td>8.20×10⁻¹⁰</td>
</tr>
</tbody>
</table>

**Solid species**

| Calcite | Calcite ↔ Ca²⁺ + CO₃²⁻ | -8.48 **| - | - |

* Obtained by using Pikal’s model [53].
** Solubility product of calcite [43].

3.1.3. Modelled Experimental setup

The experimental setup modelled was a lab-scale EKR reactor. This setup is composed of an electrokinetic cell divided in three compartments: the anolyte compartment (AC), the catholyte compartment (CC), where electrodes are located and with dimensions 15×3×3 cm, and a central compartment destined to place the polluted soil with a capacity of 675 ml (LWH: 15×15×3 cm). The level of electrolyte in compartments is constant during the tests by adding anolyte through gravity and extracting the catholyte by overflow of the CC. This modelled experimental setup has been outlined in detail in...
preceding studies [26, 36, 37]. Fig. 1 shows a scheme of the conceptual model of the setup simulated.

Figure 1. Conceptual model of the one-dimensional domain proposed for simulation. Symbols described in Appendix A.

This setup defines a one-dimensional (1D) configuration that allows reducing the computational time and provides easily interpretable results needed to understand the EKR main trends.

3.1.4. Initial conditions

The initial mass fraction of calcite in the soil was 10%. The initial electrolytes (anolyte and catholyte) are an aqueous solution of CaCO$_3$ and NaCl equilibrated with the calcite present in the soil. The same solution with an amount of clopyralid equivalent to 20 mg kg$^{-1}_{\text{soil}}$ is considered as initial porewater. The electrolyte added to the AC during the EKR test is an aqueous NaCl solution with the same pH as the initial porewater. Table 5 shows the chemical initial conditions of the different solutions used in the study.
Initially, the electrolyte compartments are filled completely and they are open to atmosphere, therefore the initial liquid pressure, $P_L$, is equal to 100 kPa (atmosphere pressure). The initial condition was an electric potential gradient equal to zero.

### 3.1.5. Boundary conditions

To solve the problem presented in this work it is necessary to define three types of boundary conditions for each of the balances presented: electrical, hydraulic and mass of dissolved chemical species. For the first case, an average electrical potential gradient of 1 V cm$^{-1}$ was applied. In the case of water mass balance, the boundary condition with the initial condition ($P_L = 100$ kPa) since the compartments are open to the atmosphere and maintain a constant level during all the cases evaluated. The boundary condition used in the mass balances of chemical species was imposed by the concentration of components in the electrolyte compartments. It is important to note that the definition of this type of boundary condition is obtained in a coupled form by means of the resolution of J-2 ordinary differential equations defining the mass balance of the chemical components in the electrolyte wells. (See Appendix A, Eq. A.11).

---

**Table 5. Chemical initial conditions.**

<table>
<thead>
<tr>
<th></th>
<th>Total components concentration / m</th>
<th>pH</th>
<th>Ionic Strength / m</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$H^+$</td>
<td>$Na^+$</td>
<td>$Ca^{2+}$</td>
</tr>
<tr>
<td><strong>Soil porewater</strong></td>
<td>3.41×10$^{-3}$</td>
<td>3.58×10$^{-3}$</td>
<td>2.49×10$^{-3}$</td>
</tr>
<tr>
<td><strong>Initial electrolyte</strong></td>
<td>3.41×10$^{-3}$</td>
<td>3.58×10$^{-3}$</td>
<td>2.49×10$^{-3}$</td>
</tr>
<tr>
<td><strong>Addition to anolyte reservoir</strong></td>
<td>-1.32×10$^{-7}$</td>
<td>3.58×10$^{-3}$</td>
<td>0</td>
</tr>
</tbody>
</table>
3.2. Simulation of EKR tests

3.2.1. Effect of calcite dissolution-precipitation process in EKR behaviour.

In this section, the importance of calcite dissolution-precipitation processes in the performance of an EKR process has been evaluated. To this end, two EKR processes have been studied: (i) the treatment of the described soil contaminated with clopyralid, in which the dissolution-precipitation processes of this mineral have been taken into account (Mineral Reaction test, MR-test) and (ii) an EKR process equivalent to the first case, in which it has been assumed that there are no precipitation-dissolution processes of calcite (no Mineral Reaction test, nMR-test). This strategy has been selected to determine the effect of these reactions on the overall performance and behaviour of the selected EKR process.

Figure 2 shows the spatial distribution of the pH in both tests for different observation times (0, 1, 2, 24 and 48 h).

**Figure 2.** pH spatial distribution at selected times. MR-test, dashed line; nMR-test, solid line.
In both tests, the pH distribution observed in the domain is characteristic of EKR treated soil. At short times (1 h), the generation of a pH gradient between the anodic (pH=3.5) and cathodic (pH=10.5) zones due to the generation of H\(^+\) in the AC and OH\(^-\) in the CC through the electrolysis of water is already observed. The transport of these ionic species through the soil generates an acidic pH front (to the cathode) and an alkaline pH front (to the anode) that collide at a point where the pH gradient is maximum. The location of this point will be very important in the discussion of results, the Maximum pH Gradient Point (M\(\text{pHGP}\)). It can be seen how the velocity with which the pH fronts move is different in the two numerical tests evaluated. The rate of advance of the acidic front is slower in the case of MR-test. This decrease is more significant at higher test times. It can be seen that after 48 hours of testing the acidic front has spread over 10.5 cm of the domain in the nMR-test, and only 7.5 cm in the MR-test. This behaviour suggests that the MR-test involves additional processes that act as a pH buffer such as the dissolution of calcite [54]. The spatial distribution of the calcite content in the MR-test is shown in Fig. 3. It is important to note that initially the calcite content is in equilibrium with the calcium carbonate concentration.
Figure 3. Spatial distribution of normalized calcite content at selected times in MR-test.

On the other hand, when the content of calcite in the soil is analysed, three areas with different behaviour can be identified. In the zone with acidic pH, between AC and MpHGP, a decrease in the initial calcite content of the soil is observed, accentuating in the zone immediately adjacent to MpHGP. The calcite dissolution process is active under these conditions, and this trend is most noticeable at higher test times (24 and 48 h) because these processes have been simulated by means of a chemical kinetic process and not by a chemical equilibrium. Meanwhile, in the soil-CC interface zone (where the cathode is located) a sudden increase in the calcite content generated by the precipitation can be seen. This behaviour has been observed (Fig. 4) in previous experimental work [55].
The third zone which was identified corresponds to the domain close to the MpHGP where the acidic and alkaline pH fronts (maximum pH gradient) are located. In this area there is an accumulation of calcite. In both the second and third zones, the observed calcite precipitation is limited only to very localize areas and not to the entire soil domain with basic pH, as would be expected. In order to understand more precisely the processes of calcite dissolution-precipitation observed in Figure 3, it is necessary to analyze the chemical speciation of the carbonate system. For this purpose, the spatial distribution of the concentration of the carbonate species ($H_2CO_3^-$, $HCO_3^-$, $CO_3^{2-}$ y $Ca^{2+}$) is shown in Fig. 5.
Figure 5. Spatial distribution of species concentration at selected times. MR-test, dashed line; nMR-test, solid line. (a) $\text{H}_2\text{O}_3^*$, (b) $\text{HCO}_3^-$, (c) $\text{CO}_3^{2-}$ and (d) $\text{Ca}^{2+}$.

Fig. 5a shows the distribution of $\text{H}_2\text{CO}_3^*$ (species including the sum of the concentrations of $\text{H}_2\text{CO}_3$ and dissolved $\text{CO}_2$) in the domain. A common trend is observed in both numerical tests, the accumulation of this species in the post-MpHGP area. This can be explained taking into account that this species is only present in systems with pH highly acid. In addition, taking into account the transport features, this species has a neutral charge, so the predominant transport mechanisms are the advective flux (hydraulic and electro-osmotic flow) and the diffusive/dispersive processes with a net flux from anode to cathode [26]. However, if we compare the spatial distributions at the same observation times, we can see how there are notable differences between the two tests analysed. In the MR-test it is observed the $\text{H}_2\text{CO}_3^*$ is present in a smaller volume of soil, which indicates that there is a relationship between the concentration of $\text{H}_2\text{CO}_3^*$ and the process
of dissolution of calcite. As Plummer demonstrated [39], this process takes place through simultaneous reactions (See Eq.5-9).

\[
\begin{align*}
CaCO_3 + H^+ & \rightleftharpoons Ca^{2+} + HCO_3^- \quad \text{Eq.(6)} \\
CO_3^{2-} + 2H^+ & \rightleftharpoons H_2CO_3^o \quad \text{Eq.(7)} \\
CaCO_3 + H_2CO_3^o & \rightleftharpoons Ca^{2+} + 2HCO_3^- \quad \text{Eq.(8)} \\
CaCO_3 + H_2O & \rightleftharpoons Ca^{2+} + HCO_3^- + OH^- \rightleftharpoons Ca^{2+} + CO_3^{2-} + H_2O \quad \text{Eq.(9)}
\end{align*}
\]

The progression of these reactions depends directly on the pH of the system and therefore on the chemical speciation of the carbonate system. [56]. In systems with strongly acidic pHs, the Eq.6 and Eq.7 reactions become important. Taking into account this reactivity, the consumption of H\(^+\) produced by the water electrolysis could justify the slowing down observed in the MR-test of the acidic front (See Fig. 2), the reduction of the calcite content by dissolution (See Fig. 3) and the increase in the concentration of H\(_2\)CO\(_3^o\) and accumulation in the area after the acidic front (See Fig. 5a). In addition, the decrease of the calcite content in the left side of the MpHGP point could be explained if it is known that the predominant reaction of the calcite solution is the Eq.6 reaction and if it is taken into account that for pH greater than 5 and with a partial pressure of CO2 greater than 0.1 atm, Eq.8 becomes important. With the contribution of the latter reaction to the general process of dissolution, the change in shape of the spatial distribution of H\(_2\)CO\(_3^o\) mentioned above can be satisfactorily described.

The second carbonate species analysed was the bicarbonate ion, HCO\(_3^-\) (Fig. 5b). This species exists at pH values between 6.3 and 10.25. For this reason, HCO\(_3^-\) is present in significant amounts only in the initial stage of the test (1 and 2 h), when the pH fronts are not very abrupt. The ion carbonate, CO\(_3^{2-}\), exhibits the opposite behavior to H\(_2\)CO\(_3^o\). The
$\text{CO}_3^{2-}$ is predominantly present in the right side of the MpHGP and has negative charge as well as $\text{HCO}_3^-$. Both species are predominantly transported by electromigration to the anode. These clarifications could explain the spatial distribution of the concentration of these species and the accumulation observed behind the MpHGP (See Fig. 5b and 5c).

Quantitatively, the MR-test presents a lower accumulation of both $\text{CO}_3^{2-}$ and $\text{HCO}_3^-$ in the area near the MpHGP since these species are, together with $\text{Ca}^{2+}$ (See reaction R.9), the drivers of the generation of calcite by precipitation (See Fig. 3). This behaviour is also observed in the area of the soil-CC interface, even at short test times (1 and 2h). This suggests that the precipitation process is faster than the dissolution process, as there is no decrease in calcite content at those times. In order to check this fact, the dimensionless reaction rate $R^*_\text{calcite}$ has been evaluated as a function of the saturation ratio, $\Omega_{\text{calcite}}$ using the expression (10) and giving the results in Figure 6.

\[ R^*_\text{calcite} = \cdot \left(1 - \Omega_{\text{calcite}}^\theta\right)^\eta \quad \text{Eq. (10)} \]

and giving the results in Figure 6.

![Figure 6. Influence of saturation ratio in dimensionless reaction rate.](image_url)
Starting from a system in equilibrium ($\Omega_{calcite}=1$), it can be observed that a decrease of $\Omega_{calcite}$ activates the process of dissolution of calcite. The rate of the calcite dissolution process has an increasing trend corresponding to the decrease of the $\Omega_{calcite}$. This evolution continues until it reaches a point where the reaction rate is stabilized at a constant value. This implies that from this point on, the dependence of the reaction rate of the dissolution process with $\Omega_{calcite}$ is negligible. Meanwhile, the precipitation process occurs when $\Omega_{calcite}$ is greater than 1. The evolution of the precipitation reaction rate as a function of $\Omega_{calcite}$ is entirely different. A roughly double log-linear increase is observed with the increase in the saturation ratio. This indicates that the precipitation rate is proportional to the concentration of species involved in that reaction (See reaction Eq.8). In this line, from a quantitative point of view, it can be observed how changes in an order of magnitude in $\Omega_{calcite}$ are translated into much more significant changes in the reaction rate in the precipitation process. This would explain the rapid calcite deposition shown in Fig. 3. Finally, the spatial distribution of Ca$^{2+}$ ion is analysed (Fig. 5d). Both tests show an accumulation of this species in the area of the CC, mainly due to the contribution of the electromigration process to the net transport of this ion [26]. The most noticeable difference between the two tests analysed is the increase in concentration observed in the acidic zone (after MpHGP) in the MR-test. This trend is according with the process of calcite dissolution observed in this zone.

Subsequently, the influence of the buffer effect generated by the dissolution of calcite on the speciation and transport of clopyralid was analysed. Two species have been considered, acid and anionic.
The pH of the soil pore water affects the chemical speciation of the substances contained in the soil [22, 57], so acidic species are present in the low pH soil zone, generally between CA and MpHGP in EKR processes. In the case studied, Clopyralid$_{\text{acid}}$ species are concentrated in this zone, favouring the transport of these species to the anodic compartment mainly by diffusion [36]. Furthermore, Clopyralid$_{\text{anion}}$ species, in equilibrium with acidic species, also accumulate in this zone and is susceptible to being

\[ \text{Figure 7. Spatial distribution of the total concentration of (a) Clopyralid$_{\text{anion}}$ species and (b) Clopyralid$_{\text{acid}}$ species at selected times. MR-test, dashed line; nMR-test, solid line.} \]
moved towards the anodic compartment mainly by electromigration [36]. For these reasons, the performance of the EKR treatment of soils with this type of pollutant (acid pollutant with anionic dissociation) improves when the volume of the acid soil zone is reduced as has been proven in previous works [36]. The buffer effect generated by the dissolution of calcite produces a reduction of the acidic zone. This is how it can be seen in Fig 7. Fig 7 shows in those locations where an accumulation of contaminant is observed (in one of the two species considered) it is always shown to a lesser extent in the MR-test.

3.2.2. Sensitivity analysis of reactive surface area in EKR behaviour.

The buffer capacity of the soil depends directly on the precipitation/dissolution kinetics of calcite, however, as previously discussed in the introduction, it is considerably complex to accurately to estimate the kinetics due to the high uncertainty associated with the reactive surface area [39]. For this reason, a sensitivity analysis of the simulated EKR process has been carried out for different values of this parameter. For this purpose, three additional MR-tests have been simulated in which a reactive surface area (\(S_{\text{calcite}}\)) value of 3.08, 10 y 100 m\(^2\) kg\(^{-1}\) \(\text{H}_2\text{O}\) (compared to the 1.54 used in the case analysed in section 3.2.1), has been assumed. The main results obtained in this study are shown in Fig. 8.
Figure 8. Sensitivity analysis of reactive surface area. Spatial distribution of the (a) of normalized calcite content, (b) pH and (c) total concentration of Clopyralid species in soil at time test of 48 h. Dynamic response of the (d) average soil pH and (e) Clopyralid removal.
From a kinetic point of view, an increase in the value of $S_{\text{calcite}}$ translates into an increase in the rate at which the dissolution and precipitation processes of calcite take place. However, qualitatively, no significant influence is found. This can be verified by analysing Fig. 8a. The behaviour observed in the cases studied is common; the same three previously identified areas with active calcite reactivity are shown (Fig. 3): (i) generalised dissolution in the acidic zone and punctual precipitation close to (ii) MpHGP and (iii) cathode. The extent to which these reactions develop is directly related to the $S_{\text{calcite}}$ value used.

Additionally, if the calcite dissolution process is specifically analyzed for a value of $S_{\text{calcite}}=100$, a decrease in the mineral content of the soil is observed and therefore the consumption of $H^+$ is more pronounced. This statement is in accordance with the pH profiles obtained in the MR-tests (Fig 8b). It can be seen that as $S_{\text{calcite}}$ increases, and therefore the kinetics of calcite dissolution, the speed of the acidic front slows down. In order to be able to evaluate the buffer capacity of the soil in global terms, the temporal evolution of the average pH has been analysed (Fig. 8d). The results obtained confirm that an increase in $S_{\text{calcite}}$ causes a significant improvement in soil buffer capacity. In the MR-test with $S_{\text{calcite}}=100$ an average pH value of 11.6 is obtained in 5 h of test, which means that in this case the acidic front is totally neutralized.

As discussed in the previous section, the pH of the porewater determines chemical speciation and, consequently, the distribution of chemical species within the soil. Therefore, the spatial distribution of the pollutant has been analysed (Fig. 8c). The neutralization of the acidic front favours the accumulation of the contaminant in the area close to the CA and therefore the transport to this compartment. An increase in the soil buffer capacity produces an improvement in the performance of the EKR process, reaching an elimination rate of close to 90% (Fig. 8e). Although these results cannot be
taken valid in any configuration and for any soil, the information obtained in this
sensitivity study is valid to show how the soil buffer capacity strongly influences the net

4. CONCLUSIONS

This paper presents a numerical study of the processes of dissolution-precipitation of
calcite in soil contaminated with clopyralid (an herbicide of the organochlorine acid type)
by using an EKR treatment. The influence of the soil buffer capacity (associated with the
dissolution of calcite) on the overall performance of the remediation process is also
studied. In addition, experimentally observed behaviours, such as rapid calcite
precipitation in the cathode electrode and the compartment where it is located, have been
identified in the simulations. Thanks to the speciation of the carbonate system, it has been
possible to improve the relative understanding of the reactive transport of these chemical
species.

In addition, the results obtained have highlighted the importance of considering the
processes of dissolution-precipitation in an EKR treatment, since the distribution of the
soil pH depends to a large extent on them. The pH of the soil porewater is a fundamental
variable in EKR treatments as it directly influences the speciation of the contaminants
(and other chemical species present) and indirectly determines the transport mechanisms
involved in the elimination of these contaminants. In the cases evaluated, it has been
proven that the buffer effect produces improvements in the overall performance of the
EKR process. The reduction of the advance of the acidic front, it favours the accumulation
of polluting species in the vicinity of the anodic compartment and can be eliminated by
means of anionic species by electromigration and of the acidic species by diffusive flux.
All these conclusions have been confirmed after a sensitivity analysis in which it has been evaluated how changes in the kinetics of the calcite dissolution-precipitation process abruptly modify the buffer capacity of the soil and therefore strongly influence the performance of the treatment. Therefore, it is very important to define accurately the kinetic parameters (specifically, the reactive surface area) since the interpretation of the results as well as the previous design of experimental setups depends on their numerical values.

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APPENDIX A

A.1. Water mass balance

Eq. (A.1) show the expression that defines the water mass balance:

\[
\frac{\partial m_w}{\partial t} + \nabla \cdot \mathbf{l}_w = 0
\]  
Eq. (A.1)

where \( m_w \) is the mass of water per unit total volume (kg m\(^{-3}\)), and it is defined as Eq (A.2), \( \nabla \cdot \) is the divergence operator, and \( \mathbf{l}_w \) is the mass flux of water (kg m\(^{-2}\) s\(^{-1}\)).

\[
m_w = \phi \cdot S_r \cdot \rho_w + \phi \cdot (1 - S_r) \cdot \rho_v
\]  
Eq. (A.2)

where \( \phi \) is the soil porosity, \( S_r \) is the degree of saturation of the soil defined by van Genuchten model [58], \( \rho_w \) and \( \rho_v \) are the liquid and vapour water density (kg m\(^{-3}\)) respectively. Vapour water density is estimated using the psychrometric equation, Eq (A.3) [59]:

\[
\rho_v = \rho_v^0 \cdot \exp\left(\frac{M_w s}{\rho_w R T}\right)
\]  
Eq. (A.3)

where \( M_w \) is the water molar mass, \( T \) is absolute temperature and, \( s \) is the matric suction, assumed equal to the capillary one (osmotic suction is not considered).

Eq. (A.4) shows the expression to calculate the flux term \( \mathbf{l}_w \):

\[
\mathbf{l}_w = \mathbf{l}_w^h + \mathbf{l}_w^{eo} = \rho_w \cdot (\mathbf{q}_w^h + \mathbf{q}_w^{eo}) = \rho_w \cdot \mathbf{q}_w
\]  
Eq. (A.4)

Where \( \mathbf{l}_w^h \) is the Darcian flux, and \( \mathbf{l}_w^{eo} \) is the electroosmotic flux, estimated with the semi-empirical model of Helmholtz-Smoluchowski [60]. The hydraulic and electroosmotic volumetric fluxes are presented as \( \mathbf{q}_w^h \) and \( \mathbf{q}_w^{eo} \) (See Eq. (A.5) and (A.7) respectively).

\[
\mathbf{q}_w^h = -K_e^h \cdot (\nabla P_L + g \cdot \rho_w \cdot \nabla z)
\]  
Eq. (A.5)
where $K^h_e$ is the effective hydraulic permeability, which is calculated by Eq (A6), $K_{sat}^h$ is the saturated permeability and $k_{rel}$ is relative permeability. $K^{eo}_e$ is the effective electro-osmotic permeability, which is estimated by Eq (A8), and $K^{eo}_{sat}$ is the saturated electro-osmotic permeability. Both relative permeability are calculated using a model Brooks and Corey [61] with an exponent of 3. Additionally, $\nabla$ is the gradient differential operator, $g$ is gravity, $z$ is the vertical coordinate, $E$ is the electric potential.

### A.2. Reactive transport

The geochemical model implemented in M4EKR module contemplates $J$ components which is capable of generating a sum of $N$ chemical species for the chemical reactions system considered (See Table 4) [62]. Thus, to determine the total chemical composition of the system, it is necessary to calculate the total mass of each component $j$ ($j=1...J$) using a general mass balance equation, Eq (A.9). However, it is not required to solve $J$ mass balances, only $J-2$ partial differential equations are necessary to compute, due to the mass of one of the components is obtained applying the electroneutrality condition and water mass is calculated by Eq. (A.1).

$$\frac{\partial m_j}{\partial t} + \nabla \cdot \mathbf{J}_j = R_j$$  \hspace{1cm} \text{Eq. (A.9)}$$

where $m_j$ is the total mass of component $j$ per unit total volume (mol m$^{-3}$), $\mathbf{J}_j$ is its total molar flux (mol m$^{-2}$ s$^{-1}$) which is defined as the sum of the contributions of four transport processes: advective transport generated by (i) hydraulic, (ii) electroosmotic and (iii)
electromigration fluxes, and (iv) Fickian diffusive-dispersive transport; and $R_j$ is its rate of production or consumption (mol m$^{-3}$ s$^{-1}$). Only $J$-2 partial differential equations are required to be resolved, due to the total mass of one of the components is computed after electroneutrality and the total mass of water is calculated by Eq. (A.1).

The resolution of the chemical speciation has been obtained applying a classical stoichiometric approach based on to solve a system of mass-balance and mass-action equations [63]. The general algorithm of this method has been described in detail in literature [52, 62, 64, 65], even so the explicit formulation utilized in M4EKR can be seen in previous works [26, 37].

A.3. Electric charge balance

The balance equation of the total electric charge is defined by the expression Eq. (A.10) assuming that the electroneutrality condition is fulfilled throughout the entire domain and the system the system is not able to accumulate electric charge.

$$V \cdot \mathbf{i} = 0$$  
Eq. (A.10)

where $\mathbf{i}$ is the total current density (A m$^{-2}$), which is estimated according Ohm's law [26, 66]. Rhoades [67] and Appelo [68] approaches are applying to calculated the apparent electrical conductivity of the soil and electrical conductivity of pore water respectively. The equations of these methods can be found in López-Vizcaíno et al. ([26]).

A.4. Mass balance in electrolyte wells

The temporal evolution of the mass of the $J$ components is obtained solving $J$-2 balance equations, Eq. (A.11) in each electrolyte compartment. The “ideal continuous stirring tank reactors” assumption is supposed in both electrolyte compartments.

$$\frac{dM_j^*}{dt} = M_{j \text{in.}}^* - M_{j \text{out.}}^* + R_j^*$$  
Eq. (A.11)
where $M_j^*$ is the total mass of component $j$ (mol) and $\dot{M}_j$ denotes the mass flow of component $j$ (mol s$^{-1}$), being an input flow (superscript $in$) or output flow (superscript $out$). Additionally, $R_j^*$ is the production/consumption/term (mol s$^{-1}$) linked to the electrochemical reactions (only water electrolysis). The superscript * indicates the kind of electrolyte compartment, which is AC or CC (anolyte or catholyte compartment respectively). The equations employed to estimate these variables can be found in a previous work [26, 36, 37].
REFERENCES


