The local chemical equilibrium (LCE) assumption has been demonstrated as a suitable approach for modeling reactive-transport processes through porous media in electrokinetic remediation (EKR) treatments. LCE can be assumed when the kinetic rates of reversible chemical reactions (in both direct and reverse directions) are fast compared to transport rates. This occurs in most aqueous-phase homogeneous systems. However, the LCE assumption could exceed the range of validity for heterogeneous reactions, such as precipitation/dissolution.

In EKR processes, the rate at which target contaminants are released from their mineral-bound forms is essential. For example, in acid-enhanced EKR treatments, the acid environment generated at the anode is exploited to dissolve the contaminant-containing minerals into mobile compounds. The progress of the acid front is generally hindered by the presence of buffering minerals, such as e.g., calcite (CaCO$_3$). Experimental results suggest that the dissolution of these carbonates, does not take place under LCE conditions.

Therefore, to further develop the prediction capability of EKR models and to understand the role of dissolution kinetics on the rate of extraction of contaminants, the kinetic rates of the “slow” reactions have to be taken into account. In this work, an EKR reactive-transport model based on Nernst-Planck (NP) equations was implemented under the LCE assumption, while taking into account the kinetic rates of the main precipitation/dissolution reactions.

For simplicity and compatibility with the reactive-transport model, the dissolution kinetics of minerals are considered function of the ion activity product. The rate of dissolution of calcite, for example, is assumed to follow the general rate law:

$$\frac{dm}{dt} = k \frac{A_0}{V} \left( \frac{m}{m_0} \right)^n$$

(1)

where $A_0$ (m$^2$) is the initial surface area of the solid, $k$ (mol m$^{-2}$ s$^{-1}$) the specific rate, $V$ (kg) the mass of solvent, $m_0$ and $m$ (mol) the amounts of solids at times $t$ and $t$, $n$ is an exponent to account for changes in $A_0/V$ during dissolution, selective dissolution and aging of the solid, $k_f$ a forward constant which accounts for $H^+$ and CO$_2$ concentrations and solvent temperature, $\text{IAP} = [\text{Ca}^{2+}]_s/[\text{HCO}_3^-]^2/P_{\text{CO}_2}$ the ion activity product, $K_{\text{calcite}} = 4[\text{Ca}^{2+}]_s^3/P_{\text{CO}_2}$, where $[\text{Ca}^{2+}]_s$ is the activity at saturation and $\sigma$ is a coefficient related to the stoichiometry of the reaction ($\sigma = 2/3$ for calcite).

We simulated the acid-enhanced EKR treatment of a model calcareous soil, consisting of an insoluble soil matrix with a certain amount of calcite. Fig. 1 compares the results in terms of pH and total Ca profiles (space and time), considering: (1) calcite dissolution under LCE and, (2) the abovementioned kinetic law. The latter case is presented by varying the parameter $A_0/V$ from 5 (bigger particles, slower rate) to 25 (smaller particles, faster rate).
In the transport model, the migrating species were \( H^+ \), \( OH^- \), \( Na^+ \), \( Cl^- \), \( Ca^{2+} \), \( HCO_3^- \) and \( CO_3^{2-} \). The simulation parameters were: an initial total Ca concentration of 1 M, tortuosity 0.4, porosity of 40%, 100% saturation, no electroosmotic flow, current density of 20 A/m\(^2\), constant soil resistivity, and catholyte maintained at pH 3 by HCl addition.

These simulations show more realistic results when chemical kinetics is included in the model. The simulations under LCE assumption produced sharp concentration and pH profiles. A front, migrating from anode to cathode, separates the regions where the calcite has dissolved completely (pH \( \approx 2 \)) from the regions where the conditions remained approximately as initial (pH \( \approx 9 \)). The transition region where calcite is being dissolved by the acid environment (pH \( \approx 5 – 9 \)) was narrow. In the simulations in which calcite dissolution kinetics was considered, the concentration and pH profiles became smoother, as the protons entering from the anodic end were not instantaneously buffered by calcite, thus penetrating further into the soil.

In conclusion, the preliminary simulation runs presented here gave a visible evidence that a reactive transport model combining LCE for fast reactions and simplified kinetic laws for slow reactions can improve the prediction capability of EKR models, without increasing significantly the number of model parameters.