

How do reaction kinetics affect electrokinetic remediation modelling results?

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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 [1]. This is the case of most aqueous-phase homogeneous systems. However, the LCE assumption could exceed the range of validity for heterogeneous reactions, such as precipitation/dissolution [2].

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 alkalinity produced at the cathode by water electrolysis is neutralized by acid addition at the catholyte and the acid environment generated at the anode is exploited to lower the pH of the system in order to dissolve the contaminant-containing minerals. The progress of the acid front is generally hindered by the presence of buffering minerals, such as *e.g.*, calcite (CaCO₃).

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.

Fig. 1 presents simulation results for acid-enhanced EKR treatment of a model calcareous soil. An insoluble soil matrix with a certain amount of calcite was considered. The rate of dissolution of calcite was assumed to follow the general rate law [3,4]:

$$\frac{dm}{dt} = k \frac{A_0}{V} \left(\frac{m}{m_0} \right)^n, \quad k = k_f \left[1 - \left(\frac{\text{IAP}}{K_{\text{calcite}}} \right)^\sigma \right] \quad (1)$$

where A_0 (m²) 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 θ 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 CO₂ concentrations and solvent temperature, $\text{IAP} = [\text{Ca}^{2+}][\text{HCO}_3^-]^2/P_{\text{CO}_2}$ 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 σ is a coefficient related to the stoichiometry of the reaction ($\sigma = 2/3$ for calcite).

Fig. 1 compares the results in terms of pH and total Ca profiles (space and time) for the simulations performed considering (1) the calcite dissolution under LCE and, (2) the abovementioned kinetic law. The latter case is presented for two different scenarios, using the parameter $A_0/V = 25$ (smaller particles, faster rate) and $A_0/V = 15$ (bigger particles, slower rate). In both runs the value of $n = 2/3$ was assumed for the exponent, corresponding to spherical calcite particles.

In the NP transport model, the migrating species were H^+ , OH^- , Na^+ , Cl^- and Ca^{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 linear voltage gradient. The length of the soil column was 30 cm and the area 50 cm^2 . The catholyte was maintained at pH 3 by HCl addition. The time step was 600 s.

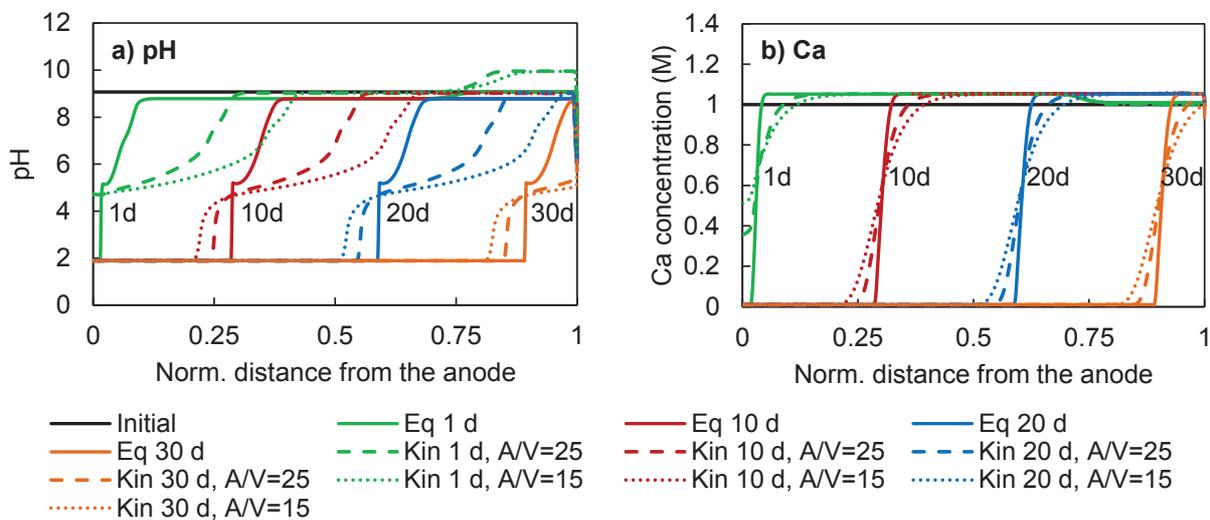


Fig. 1. Comparison between EKR simulations with and without calcite kinetics. (a) pH profile evolution with time, (b) Ca (total concentration) profiles

These simulations show more realistic results when chemical kinetics are considered. 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 the calcite is being dissolved by the acid environment ($pH \approx 5 - 9$) was narrow. In the second set of simulations, in which chemical kinetics for the dissolution of calcite was considered, the concentration and pH profiles got smoother, as the protons entering from the anodic end were not instantaneously buffered by the calcite, thus penetrating further into the soil.

In conclusion, the preliminary simulation runs presented herein 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.

References

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