Physicochemical and numerical modeling of electrokinetics in inhomogenous matrices - DTU Orbit (17/01/2019)

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An electric field externally applied to a porous material, results in mobilization of chemical species through the electrolyte and transport of the pore solution itself. Based on this, several techniques have been developed aiming at removing of selected contaminants or injecting specific compounds into porous solid matrices of different kinds. These techniques are typically denoted as electrokinetic treatments.

In these kind of electrochemically induced transport processes, the driving force is related the concentration gradients and the unbalanced in ionic charge produced by the electrochemical reactions taking place at the electrodes as a consequence of the applied electric field. Additionally, non-electroneutral electric double-layers at the interfaces between electrolyte and solid surfaces are affected by the induced electric potential, resulting in electrokinetic transport.

In addition to the electrochemical reactions, these kinds of transport processes are strongly influenced by the chemical interactions between the species present in the heterogeneous system, either dissolved in the electrolyte, precipitated or adsorbed at the solid surface.

Physicochemical models form a necessary basis for the understanding of the involved processes and the development of a theoretical framework able to take into account the complex interactions taking place in any electrokinetic or electrochemically induced process. The mathematical solution, normally by means of computer-aid numerical methods, allows the corroborations of the assumptions and, eventually, the development of prediction tools for optimizing the different treatments.

In accordance to this, the primary objectives proposed for the present project "Physicochemical and numerical modeling of electrokinetics in inhomogeneous matrices" are:

1. to formulate a fundamental theory that mathematically explain the physicochemical processes taking place during electrokinetic treatments
2. to build a reliable and accurate numerical model which enables the prediction of the desired effects and the side effects effects in and on the materials from the treatments

A physicochemical model has been proposed based on the Nernst-Planck-Poisson system. The model includes the transport of water through the porous media, the monitoring of the degree of saturation, the pH value and the porosity throughout the domain; and a comprehensive set of chemical and electrochemical reactions involving solid, gaseous and aqueous species and water in both the electrolyte and the solid structure. This coupled reactive-transport model, covering such a number of physical and chemical aspects in the process, is assumed an innovative contribution to the state of the art of modeling of electrokinetics processes. Furthermore, the physicochemical model is described in a generalized manner, so it can be used to simulate a wide range of electrokinetic treatments for different inhomogeneous matrices.

A numerical model has been built forthemathematicalsolutionoftheproposed physicochemical model. The numerical model is mainly based on a finite elements method for the integration of the transient system of partial differential equations coupled with a Newton-Raphson method for computing chemical equilibrium.

During the development of the proposed physicochemical and numerical model, different electrokinetic systems have been studied. Some worth mentioning investigations and the results drawn from the simulations are summarized below.

1. The electro-desalination treatment of bricks and other construction materials using a buffer substance enhancement was studied. Simulation-based analysis showed good prediction of the removal efficiencies and rates for chlorides nitrates and sulfates. Simulation threw light on some aspects not easily observed experimentally, such as the chemical species distribution throughout the process or the possibility of precipitation of salts within the porous structure. It was found, for example, that formation of gypsum is a limiting factor in the desalination of sulfate-contaminated bricks or stones, and that there is a connection between the presence of magnesium and the capacity of buffering the alkaline front produced in the cathodic reaction.
2. Using the chemical equilibrium model or the reactive-transport combined model, some feasibility studies for the mobilization of specific contaminants were carried out. For example, speciation analysis of Pb in soil was studied for the selection of different extracting agents in order to design a combined acid enhanced with selective chelators EK treatment. Different extracting agents were tested using the speciation numerical model, such as EDTA, acetic acid, citric acid and nitric acid. Results showed that citric acid and EDTA are the extracting agent which increase more the solubility of Pb in soil, and that the efficiency of the process is strongly limited by the buffering capacity of the soil itself, not only because it determines the pH value, but also because there is a tendency of forming calcium citrate insoluble lead carbonate.
3. The proposed model was used for the simulation-based analysis of the transient formation of the diffuse layer of the electric double layer in the vicinities of a reactive surface. In this case, the model was adapted to simulate a microscale system. Concentration profiles of the ionic species in the diffuse layer were obtained, satisfying not only the electrical balance between the electrolyte and the surface charge, but also the chemical equilibrium condition between the chemical species in the electrolyte. Apart from this new approach for the distribution of species under chemical equilibrium conditions, some conclusions were drawn from the simulations. For example, concentration profiles for the non-ionic species are formed at the vicinities of the charged surface as a result of the chemical interaction with the ionic species in the system. Results also show that the transient formation of electric double layers may be controlled by the kinetics of the surface reactions, and not by the electro-diffusion transport process.

The results summarized here are just a sample of the many possibilities offered by the simulation-based analysis that can be obtained using the proposed physicochemical and numerical model.