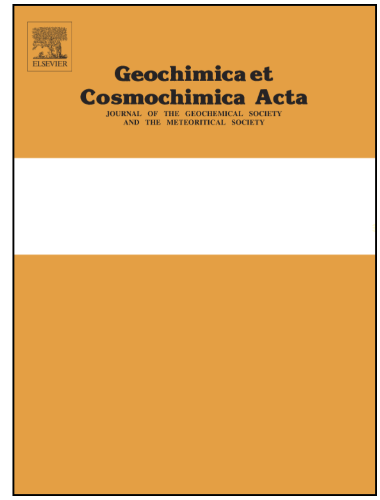

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Simulating Donnan equilibria based on the Nernst-Planck equation

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Abstract

Understanding ion transport through clays and clay membranes is important for many geochemical and environmental applications. Ion transport is affected by electrostatic forces exerted by charged clay surfaces. Anions are partly excluded from pore water near these surfaces, whereas cations are enriched. Such effects can be modeled by the Donnan approach. Here we introduce a new, comparatively simple way to represent Donnan equilibria in transport simulations. We include charged surfaces as immobile ions in the balance equation and calculate coupled transport of all components, including the immobile charges, with the Nernst-Planck equation. This results in an additional diffusion potential that influences ion transport, leading to Donnan ion distributions while maintaining local charge balance. The validity of our new approach was demonstrated by comparing Nernst-Planck simulations using the reactive transport code Flotran with analytical solutions available for simple Donnan systems. Attention has to be paid to the numerical evaluation of the electrochemical migration term in the Nernst-Planck equation to obtain correct results for asymmetric electrolytes. Sensitivity simulations demonstrate the influence of various Donnan model parameters on simulated anion accessible porosities. It is furthermore shown that the salt diffusion coefficient in a Donnan pore depends on local concentrations, in contrast to the aqueous salt diffusion coefficient. Our approach can be easily implemented into other transport codes. It is versatile and facilitates, for instance, assessing the implications of different activity models for the Donnan porosity.

Keywords: Donnan model, clay, montmorillonite, ion transport, coupled transport, reactive transport, Nernst-Planck, electrochemical migration, anion exclusion, salt diffusion coefficient

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