

Simulating Donnan equilibria based on the Nernst-Planck equation

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Transport of ions through clays and clay membranes is an important process in many industrial and engineering applications. A proper modelling of ion transport in clays is especially essential when assessing the performance of planned disposal sites for nuclear waste, because claystones are widely considered as potential host rocks, and clayey materials such as bentonite are used to construct engineered barrier systems. Negative surface charges of clay particles exert electrostatic forces that then affect transport of charged species through clays. As a result, anions are partly excluded from pore water near the charged surfaces, whereas cations are enriched within these regions. At the pore scale, the gradual depletion or enrichment of ions near a charged surface can be modelled by the Poisson-Boltzmann equation. This equation can be solved for specific geometries of single surfaces and simple electrolytes, leading to a diffuse layer of charges compensating those of the solid surface. For instance, solving it for a symmetric electrolyte and a single planar charged surface leads to the Gouy-Chapman diffuse double layer model. Triple layer models including an additional innermost layer of more strongly bound cations of finite size were also developed (e.g., the modified Gouy-Chapman model). Applying the Poisson-Boltzmann equation to real clay samples and complex solution chemistry, however, is computationally expensive and would, in principle, require a detailed knowledge of the geometry of the pore space.

The Donnan approach can be used as an alternative to model the average ion composition in pore water affected by surface charges. This approach is more consistent with the continuum scale that is typically used for modelling transport through rocks at larger scales. The Donnan approach is based on equating the chemical potentials in an external pore water, which is unaffected by surface charges, and in the internal pore water that is uniformly affected by the surface charges. In this way, effects of anion exclusion from the pore water and cation enrichment within the pore water can be modelled in a coupled simulation. At present, the two geochemical transport codes Phreeqc and CrunchFlowMC can consider such Donnan equilibria in transport simulations explicitly. They both follow a double porosity approach, in which the pore space of a clay is split into a charge-free (called free, or macro) porosity and a Donnan (called diffuse layer, or micro) porosity. For that purpose, the codes had to be modified considerably. Routines were also written to couple other transport codes that do not consider diffuse layers explicitly to Phreeqc or CrunchFlowMC to make use of this specific feature, which also required major programming efforts.

Here we introduce an alternative way to represent Donnan equilibria without explicit Donnan modifications: We consider charged surfaces as immobile components of the pore solution and use the Nernst-Planck (NP) equation to simulate coupled transport of all components, including the immobile ions. The coupling between transport of mobile and immobile ions leads to the development of a diffusion potential between internal and external pore water. At steady state, it equals the Donnan potential and affects anion and cation concentrations according to the Donnan equations. The validity of our new approach is demonstrated with the geochemical code Flotran. We compare simulation results obtained with Flotran including immobile anions with analytical Donnan solutions available for simple systems, and with results obtained with CrunchFlowMC with its explicit Donnan formulation. At steady state, a perfect agreement is obtained for a single symmetric electrolyte (NaCl) as well as for a single asymmetric electrolyte (CaCl_2). We furthermore show that the standard numerical evaluation of the electromigration terms in the NP equation leads to erroneous results for asymmetric electrolytes and propose an alternative evaluation leading to correct results.

Our new approach to model Donnan equilibria is promising because it can easily be implemented into other codes that can handle multi-component diffusion based on the NP equation, thus eliminating the need for strong code modifications. It is possible to consider a single Donnan pore space in the clay, or also two parallel porosity domains as in the dual porosity codes Phreeqc and CrunchflowMC, as well as a partial shielding of surface charges by a Stern layer. Furthermore, it allows testing or modifying various assumptions regarding ion transport in the diffuse layer, such as those related to the importance or the values of activity coefficients for ions within the Donnan space.