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Predicting cation diffusion coefficients in clays and clay rocks

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Clay rocks are considered in several European countries as potential host rock formations for the underground disposal of radioactive waste. Because of their very low hydraulic conductivities, spreading of radionuclides through such formations may predominantly occur by molecular diffusion. Many experimental studies are thus being performed to investigate the diffusion of cations and other potential contaminants through various clay rocks as well as through pure swelling clays that may be used as additional buffer material.
Whereas determining the diffusion properties of mobile tracers like tritiated water can be done within reasonable time, the measurements involving sorbing tracers are more complex and very time-consuming. It is thus tempting to determine diffusion coefficients of sorbing cations in an indirect way from more readily measurable quantities and based on cation diffusion coefficients measured for other materials. Various models exist that try to estimate cation diffusion coefficients from parameters like the bulk density, the porosity or the pore sizes of the rock, and the sorption distribution coefficient. In some models, an average mobility of cations that are sorbed on clay surfaces is in addition required, whereas other models rely on a constrictivity factor for transport in the interlayer space of the clays.
In this contribution, we outline the differences and the commonalities of such models regarding some key parameters. We then compare model estimates with measured data from the literature, with a special emphasis on the associated uncertainties. Because some of the required parameters, notably the surface mobilities as well as the interlayer constrictivities, have typically large uncertainties, it is difficult to judge which model is best suited. However, it seems that several models can be used to set reasonable limits for cation diffusion coefficients in clay rocks that have not been investigated so far.