8–8 Mechanistic Modeling of Nuclide Migration in Rock
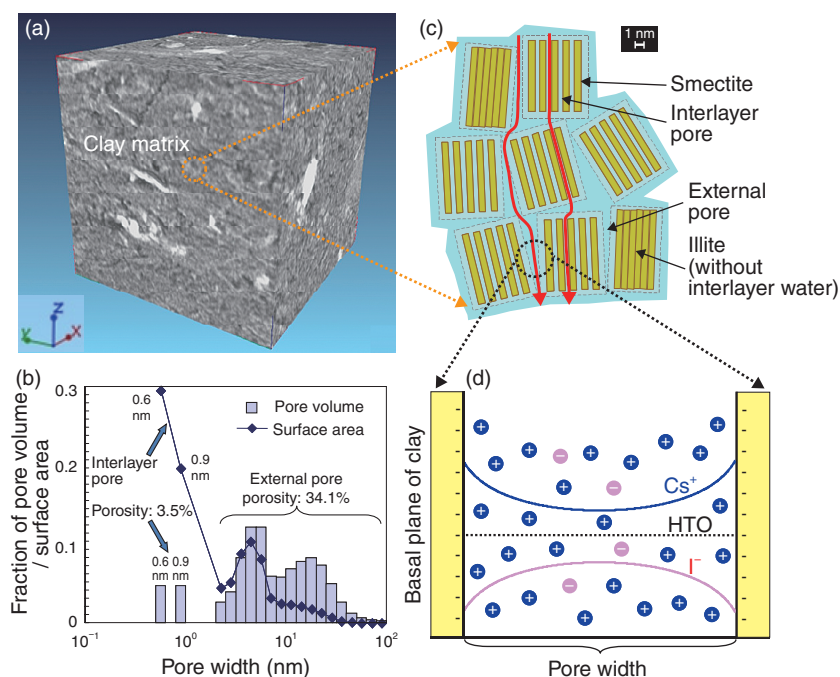## — Clay-Based Modeling Approaches for Diffusion and Sorption in Mudstone —

Fig. 8-20 Conceptual images of a clay-based diffusion model
(a) 3D image of a rock matrix obtained by X-ray CT; (b) pore-size distribution by mercury porosimetry; (c and d) simplified sketches of the clay matrix and EDL in a nanoscale pore.
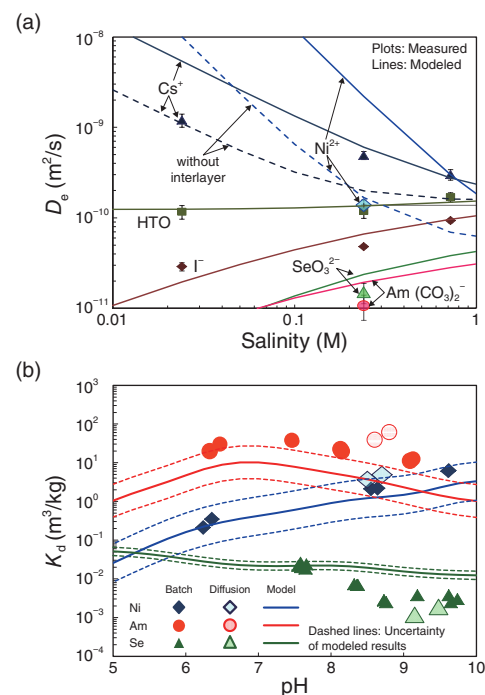

Fig.8-21 Comparison between measured and modeled results of Ni, Am, and Se
(a) D_e vs. pore-water salinity; (b) K_d vs. pH.

Diffusion and sorption of radionuclides (RNs) in rocks are key processes for the safe geological disposal of radioactive waste. To set reliable parameters for various geological and geochemical conditions relevant to safety assessment, understanding diffusion and sorption processes and developing mechanistic models is necessary. A clay-based modeling approach that assumes key contributions of clay minerals has been developed to describe the diffusion and sorption behavior of simple ions (Cs^+, I^-) in the mudstone from the Horonobe underground research laboratory (URL) in previous studies. The present study focuses upon experimental and numerical investigation of the diffusion and sorption of more complex species including Ni(II), Am(III), and Se(IV) in the mudstone from the Horonobe URL.

Effective diffusivities (D_e) measured by through-diffusion experiments indicated cation excess and anion exclusion effects and were interpreted by the clay-based modeling approach. The diffusion behaviors were assumed to be dominated by nanoscale pores in the homogeneously dispersed clay matrix, based on mineral and pore distributions by nano-focus X-ray CT and mercury porosimetry (Figs.8-20(a) and (b)). The clay matrix comprises non-swelling illite without interlayer water and swelling smectite with interlayer water (Fig.8-20(c)). The diffusion model based on the electrical double layer (EDL) describing the relative ionic concentrations and viscoelectric effects at the negatively charged clay surface is connected to a simplified homogeneous-pore model with the size distribution (Fig.8-20(d)). The dominant species under the test conditions are estimated to be Ni^{2+}, $Am(CO_3)_2^-$, and SeO_3^{2-}. The diffusion model can qualitatively express D_e trends including cation excess and anion exclusion effects ($Cs^+ > Ni^{2+} > HTO > I^- > SeO_3^{2-} > Am(CO_3)_2^-$), as well as the salinity dependences (Fig.8-21(a)). As shown by dashed lines in Fig.8-21(a), interlayer pores contribute significantly to cation diffusion, and the disparity between the modeled and measured D_e values of cations may indicate that the contributions of the interlayer pores vary according to cations and salinity conditions.

Distribution coefficients (K_d) measured by batch sorption experiments were consistent with those obtained by diffusion tests and were calculated by the sorption model using site capacities determined from the clay contents and model parameters (i.e., ion exchange and surface complexation). Trends in K_d predicted by the sorption model, considering the additive contributions of illite and smectite, demonstrate reasonable agreement with measurements as a function of pH (Fig.8-21(b)).

From these results, electrostatic interactions in nanoscale pores and sorption reactions at clay surfaces control the diffusion and sorption of various RNs. The clay-based modeling approach can be applied to predicting the diffusion and sorption behaviors of various RNs with complex chemistry in mudstone.

Reference

Tachi, Y. et al., Clay-Based Modeling Approach to Diffusion and Sorption in the Argillaceous Rock from the Horonobe URL: Application to Ni(II), Am(III), and Se(IV), The Clay Minerals Society Workshop Lectures Series, vol.21, chapter 19, 2016, p.241-250.