MODELING THE ACID-BASE SURFACE CHEMISTRY OF MONTMORILLONITE

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Proton uptake on montmorillonite edge surfaces can control pore water pH, solute adsorption, dissolution kinetics and clay colloid behavior in engineered clay barriers and natural weathering environments. Knowledge of proton uptake reactions, however, is currently limited by strong discrepancies between reported montmorillonite titration data sets and by conflicting estimates of edge structure, reactivity and electrostatics. In the present study, we show that the apparent discrepancy between titration data sets results in large part from the widespread use of an erroneous assumption of zero specific net proton surface charge at the onset of titration. Using a novel simulation scheme involving a surface chemistry model to simulate both pretreatment and titration, we find that montmorillonite edge surface chemistry models that account for the “spillover” of electrostatic potential from basal onto edge surfaces and for the stabilization of deprotonated Al-Si bridging sites through bond-length relaxation at the edge surface can reproduce key features of the best available experimental titration data (the influence of pretreatment conditions on experimental results, the absence of a point of zero salt effect, buffer capacity in the acidic pH range). However, no combination of current models of edge surface structure, reactivity and electrostatics can quantitatively predict, without fitted parameters, the experimental titration data over the entire range of pH (4.5 to 9) and ionic strength (0.001 to 0.5 mol dm⁻³) covered by available data.

Figure 1: Montmorillonite acid-base titration data of Baeyens and Bradbury (1997) and Duc et al. (2005) simulated with a model that accounts for the influence of montmorillonite pretreatment on the net proton surface charge at the onset of titration.

References:

