Thermodynamic Analysis of Chalk–Brine–Oil Interactions

The surface complexation models (SCMs) are used successfully for describing the thermodynamic equilibrium between the pure calcite surface (carbonate and calcium sites) and brine solutions. In this work, we show that the model parameters that are reported for the calcite–brine system are not applicable to the natural carbonates. We adjust the SCM reaction equilibrium constants by fitting the model to the ζ potential data that are reported for the pulverized Stevns Klint chalk. Then, we use the model, implemented in the PhreeqcRM geochemistry package coupled with a finite volume solver, to predict the breakthrough composition of different ions in the chromatographic experiments on the intact Stevns Klint chalk cores. Again, the model falls short in predicting the reactive transport of brine in a natural carbonate, implying that ζ potential data is not enough for optimizing the SCM model parameters for the reactive transport applications. We propose an optimization procedure that fits the coupled SCM–transport model parameters to the chromatographic (single-phase core flooding) data. The ζ potential measurements are implemented in the optimization scheme as nonlinear constraints. We then use the optimized model to study the thermodynamic equilibrium between the oil and chalk surfaces in the presence of different brine compositions, including the dissolution and precipitation of minerals. We represent the chalk–oil interactions by acid–base equilibrium reactions between the calcium and carbonate sites on the chalk surface and carboxylic acids and amine bases on the oil surface, respectively. Comparing the model results to a data set of the spontaneous imbibition experiments for chalk shows that the remaining oil saturation in the imbibition experiments is correlated with the number of bonds between the amine and carboxylate groups on the oil surface and the carbonate and protonated calcium on the chalk surface.