Simulation of fluid-mineral kinetic reactions during CO2 storage using ChemApp and SUPCRT92 coupled to OpenGeoSys

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After CO_2 is injected into a deep underground saline formation, the initial geochemical equilibrium state is changed, and a series of geochemical reactions between CO_2, the pore fluid and the minerals present is initiated. Most of these geochemical reactions are kinetically controlled. For example, dissolution and precipitation of carbonates and silicates have to be considered as kinetic reactions, as the reaction time scale exceeds the transport timescale. The geochemical reactions and the flow and transport processes in the saline formation thus interact in a complex way, influencing each other. The geochemical kinetic reactions depend on the composition of the fluids present and the mineral composition. For the required kinetic rate laws, adequate parameters are required. These parameters fall into two groups, i.e. specific kinetic parameters which depend on the individual kinetic rate law used, as well as thermodynamic parameters, such as reaction equilibrium constants and activity coefficients of each species involved in the reaction system. Equilibrium constants depend on temperature and pressure conditions, activity coefficients of individual species depend on the system composition. During a coupled reactive transport simulation, the change of these factors requires that these thermodynamic parameters must be constantly updated. In order to calculate these necessary parameters, we coupled two geochemical models, ChemApp and SUPCRT92, to the multi-phase flow and transport simulator OpenGeoSys. Based on the Gibbs free energy minimization method, ChemApp calculates activity coefficients of individual species and equilibrium constants for each given geochemical kinetic reaction. The SUPCRT92 program calculates thermochemical properties of all species involved at various temperature and pressure conditions as well as solution compositions using Helgeson-Kirkham-Flowers equations and databases. Based on the HKF equations, the SUPCRT92 program has been widely applied in reactive transport simulations.

This study reports the implementation and verification of the multi-component transport code OpenGeoSys coupled with simulation of kinetic mineral reactions, where the basic thermodynamic properties are obtained either by ChemApp or SUPCRT92. The coupled simulator is verified by comparison against Phreeqc and other software. Benchmarks as well as code verifications are presented. We then use our code to study reactive transport problems in CO_2 geological storage systems. Especially, the kinetics of dissolution and precipitation reactions of carbonate and silicate minerals due to CO_2 fluid migration can be simulated. Using data from the Michigan Basin which is composed primarily of calcite and dolomite, we study the kinetic reactions between fluid and cap rock and compare our simulation results with experimental data to demonstrate the ability of our simulation program for an assessment and prediction of CO_2 geological storage. We compare the two equilibrium geochemical methods and report the differences and their reasons.